A HIGHWAY OF POLLUTION WITH NO BOUNDARIES: A STUDY USING LEAD ISOTOPE RATIOS IN WET DEPOSITION AND LICHEN TO TRACE ATMOSPHERIC POLLUTION

by
Tamra Akerman

A thesis submitted as a partial
requirement in the
Master of Science (MSc) in Chemical Science

Faculty of Graduate Studies
Laurentian University
Sudbury, Ontario

THESIS DEFENCE COMMITTEE/COMITÉ DE SOUTENANCE DE THÈSE
Laurentian Université/Université Laurentienne
Faculty of Graduate Studies/Faculté des études supérieures

Title of Thesis Titre de la thèse	A HIGHWAY OF POLLUTION WITH NO BOUNDARIES: A STUDY USING LEAD ISOTOPE RATIOS IN WET DEPOSITION AND LICHEN TO TRACE ATMOSPHERIC POLLUTION
Name of Candidate Nom du candidat	Akerman, Tamra
Degree Diplôme	Master of Science
Department/Program Département/Programme	Chemical Sciences
Date of Defence Date de la soutenance	April 17, 2015

APPROVED/APPROUVÉ

Thesis Examiners/Examinateurs de thèse:

Dr. Graeme Spiers
(Supervisor/Directeur de thèse)

Dr. Peter Beckett
(Committee member/Membre du comité)

Dr. Francois Caron
(Committee member/Membre du comité)

Dr. Michael Ketterer
(External Examiner/Examinateur externe)

Approved for the Faculty of Graduate Studies
Approuvé pour la Faculté des études supérieures
Dr. David Lesbarrères
M. David Lesbarrères
Acting Dean, Faculty of Graduate Studies
Doyen intérimaire, Faculté des études supérieures

ACCESSIBILITY CLAUSE AND PERMISSION TO USE

Abstract

To fingerprint lead deposition over approximately a two year timeframe, possible variationsin the sources of lead pollution over Northern Ontario was investigated by collecting snowpack, rainwater and lichen. The collection of samples was along two main transects: A West East transect between Sault Ste. Marie and Sudbury; and a South North transect from Sudbury up through Timmins to Kapuskasing. Sample collection along these two transects was conducted during the summer of 2009 and during the Shutdown of Vale Inco's Smelter in the winter month of January 2009. The objective was to determine if Pb anthropogenic pollution from major point sources in northern Ontario (Essar Steel Algoma, Xstrata Sudbury Smelter Operations, Xstrata Kidd Metallurgical Plant) could be traced using isotopic ratios. As a result the Pb isotope fingerprint in northern Ontario can be explained by a binary mixing of anthropogenic emissions from northern Ontario refining operations and coal fired power plant emissions that are transported with prevailing winds from the Ohio Valley. Major point sources showed distinct differences in signatures and samples that were not collected in proximity to a point source were diluted and greatly influenced by the U. S signature.

Keywords

Lead, Isotopes, Pollution, Refining, northern Ontario, Coal Power, Fingerprint, Bio-monitoring, Rainwater, Snowpack, Lichen. Smelter

Acknowledgements

I would like to thank my advisor, Dr. Graeme Spiers for your patience and help over the last couple years. I would like to thank my advisory committee members Dr Peter Beckett, Dr Francois Caron and Dr. Balz Kamber.

Thank you to all my family, friends and work colleagues for all their support and input. Thank you Pamela Koski and Jen Hargreaves and the other many graduate students for many cold road trips and trekking out in the woods to get snow and rain samples.

I would also like to acknowledge Laurentian University and MIRARCO for their support in the funding of the project. In particular MOE for providing funding for the MOSS project which was a major aspect of the moss sampling (P.I. Spiers and Beckett).

I would also like to thank the Elliot Lake Research Centre and Penguin for letting me use their facilities.

Table of Contents

List of Tables

List of Figures

List of Plates

List of Appendices

1.0 Introduction

1.1 Lead in the Atmosphere

The atmosphere is an important geochemical receptor and transport medium for trace metals emitted from ground based sources (Church, 1994). Natural lead, or lead from non-radiogenic sources within the earths crust, is found in soils, plants and water (Crook, 1921). Metallic lead in nature is very rare, with the element lead being commonly found in such ore minerals such as galena (PbS), cerussite (PbCO3) and less commonly in anglesite ($PbSO_4$) and pyromorphite ($Pb_5(PO_4)_3Cl$) (Crook, 1921). The large majority of lead is not derived from ores specifically mined for their Pb content, but originates as a co-product from the extraction of copper, zinc, nickel and silver containing ores. In northern Ontario and many other places around the world, anthropogenic activities can significantly alter the chemical and isotopic composition of lead in the atmosphere (Mart, 1983). Anthropogenic activities are primarily responsible for the enrichment of many trace elements now found in the atmosphere.

1.2 Origin of Lead in Ontario

The origin of Ontario's major emissions and thus atmospheric enrichments in lead are listed in Table 1 as reported from the 2009 national pollution release inventory (Canada, 2009). The non-ferrous smelting and refining industrial operations are the main sources of lead emissions in Ontario.

Table 1. NPRI 2009 Ontario Lead Emissions Data Showing a Massive Contribution from the Non-Ferrous Smelting and Refining Industry

Industrial Sources	Lead (Kg's)
Iron and Steel Industries	**$2.3x10^3$**
Primary (Blast furnace and DRI)	$7.8x10^2$
Secondary (Electric Arc Furnaces)	$1.5x10^3$
Non-Ferrous Smelting and Refining Industry	**$3.8x10^4$**
Primary Ni, Cu, Zn, Pb	$3.8x10^4$
Secondary Pb, Cu	$3.5x10^2$
Electric Power Generation (Utilities)	**$5.5x10^2$**
Coal	$4.6x10^2$

Table 2 shows emissions from the major coal fired power plants in Ontario as reported from the 2009 National Pollution Release Inventory.

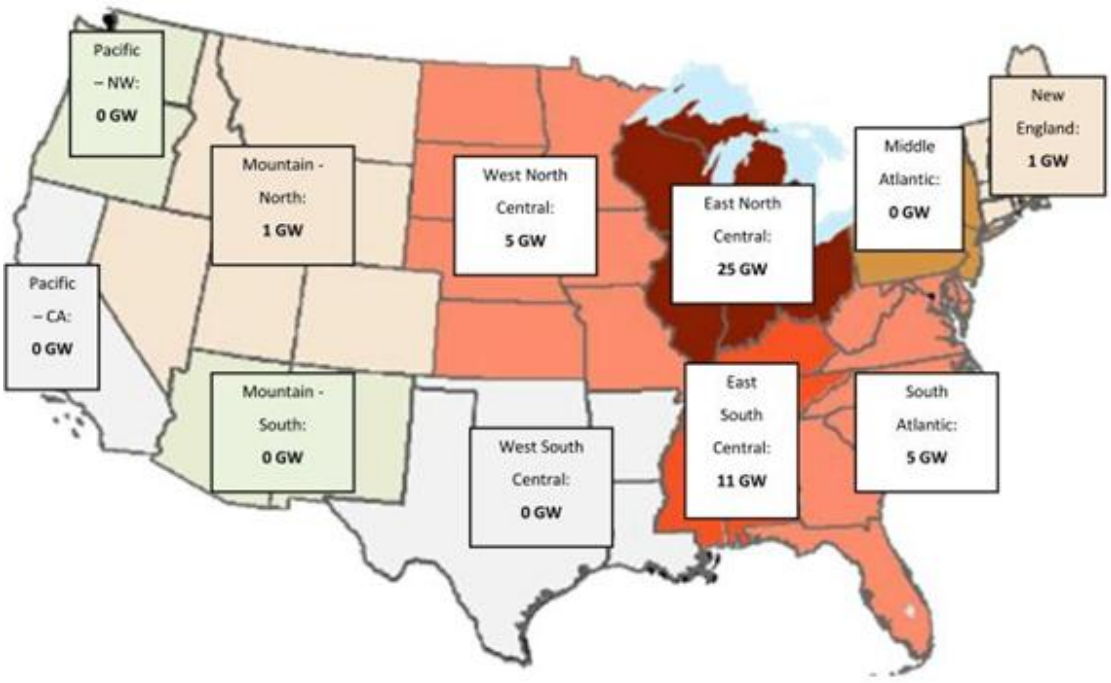
Table 2. 2009 NPRI Data Showing the Minimal but still Significant Lead Emissions from Coal Fired Power Plants in Ontario

Company	Lead (Kg's)
Ontario Power Generation Locations	
Nanticoke Generating Station	$2.5x10^2$
Lambton Generating Station	$2.1x10^2$
Thunder Bay Generating Station	2.7
Atikokan Generating Station	1.5
Lennock Generating Station	$2.6x10^{-2}$
Total	**$4.6x10^2$**

The quantity of lead emitted by the power generation industry at 464.23 kg per annum seems insignificant, especially in comparison to the overall emission load in northern Ontario.

1.3 Trans boundary Lead

As air pollution is a trans boundary issue with air masses transporting fine aerosolic particles from the point of origin, the emitted contaminants do not necessarily contaminate the environment in the country of origin. Therefore, in the overall Northern America perspective, the trans-boundary pollution from the western states coal fired power plants make coal a very serious contributor, with pollution carried by prevailing winds up through the Ohio Valley to the north-east Canadian air sheds. Air quality impacts from large scale coal-powered electrical generation facilities in the Midwestern States are not only a concern



for the northern Ontario population, but are of concern globally. Figure 1 shows neighboring states and their annual power production generated from coal fired power plants.

Plate 1 Neighboring American States and Respective Coal Fired Power Plant Electricity Production (International, 2011)

The power generation is concentrated primarily in the Ohio Valley, Upper Midwest, Mid-Atlantic, and Southeast states. Table 3 lists Pb emissions from coal fired power plants in East North Central and the Middle Atlantic States. These states are those highlighted in dark red and yellow in Figure 1 as reported by the U.S Environmental Protection Agency's 2008 national emission inventory.

Table 3. Northern Ontario Prevailing Wind Pb Emission Sources from Coal Fired Power Plants in the East North Central and Middle Atlantic States (Agency, 2008).

State	Sector	Pb Emissions (kg)
Illinois	Coal Fuel Combustion	4.79×10^3
Indiana	Coal Fuel Combustion	5.14×10^3
Michigan	Coal Fuel Combustion	4.52×10^3
Ohio	Coal Fuel Combustion	8.67×10^3
Wisconsin	Coal Fuel Combustion	1.27×10^3
Total		**2.44×10^4**

The total Pb emissions from Table 3 is 2.44×10^4 tons. This is the major source of Pb transported into northern Canada as the atmosphere is not divided by barricades separating provinces or countries, but is rather a highway of pollution spanning large distances that needs to be monitored, with emissions reduced not only locally but by our friendly neighboring donor nation to the south. The percent of transboundary transportation is unquantifiable due to impacts from various other Pb contributors.

1.4 Pb Health Effects

The determination of both fate and the source of lead in the environment is of great importance because the higher the level and potential dose, the greater the risk for associated health problems. Pollution with lead from industrial processes, as well as from natural sources, is a very serious environmental problem and can pose a major threat to the health and wellbeing of people both locally and globally. The basic objective in the field of air pollution control is to restrict the concentration of pollutants such as lead in the ambient air to such levels that will not adversely affect the health, wellbeing or welfare of the ecosystem and/or the community. The USEPA's health based national air quality standard for lead is 1.5 micrograms per cubic meter [measured as a quarterly average] (Sturm, 2011). Lead is a toxic heavy metal that can enter the human body through inhalation and ingestion from a variety of sources such as contaminated air and water, soil and food. Lead can build up in the body in bone, blood and soft tissue. Being readily excreted, lead can also affect the kidneys, liver, nervous system, and other organs (Sturm, 2011). Exposure to high doses of lead can cause serious health problems for adults including anemia, kidney disease, reproductive disorders, and neurological impairments (Sturm, 2011) The risk for children is worse because in addition they can have a loss of development skills, hearing loss, kidney damage and slowed body growth to name a few (Perez, 2011). By monitoring the environmental releases from point sources to environmental media, authorities can foresee and prevent threats and risks before they become problems.

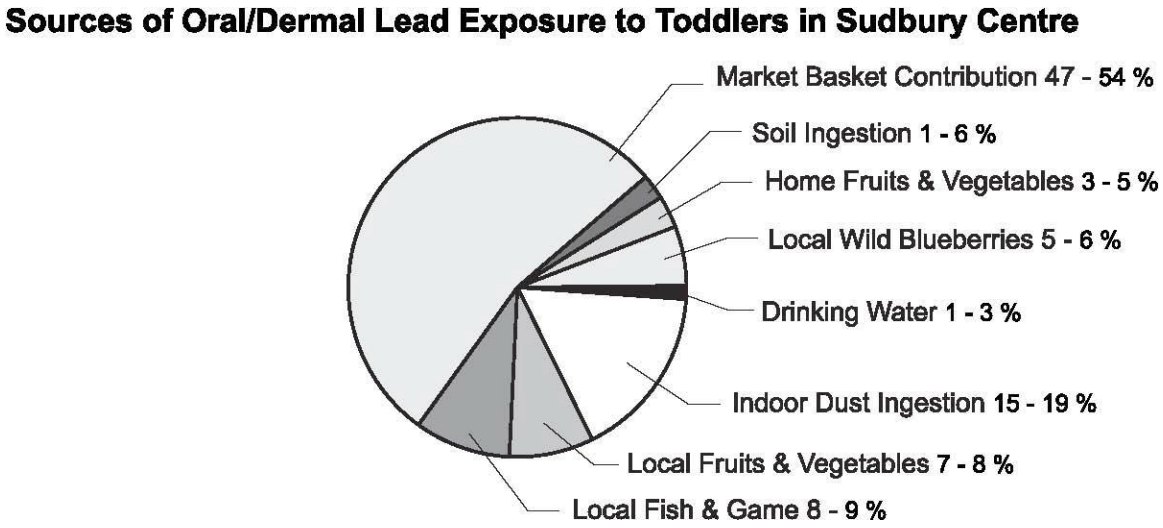
1.4.1 A Pb Health Study conducted in Sudbury, Ontario

While the current risk calculated for typical exposures to lead within the Sudbury area are inside acceptable limits, levels of lead measured in some soil samples indicate a potential risk in localized areas of Copper Cliff, Coniston, Falconbridge and Sudbury Centre. This section

addresses the following findings related to lead from the Sudbury Area Risk Assessment (SARA) Human Health Risk Assessment (-HHRA) report (SARA Group, 2001):

"The risks calculated for typical exposures to lead in the environment throughout the Greater Sudbury area are within acceptable benchmarks for protection of human health. However, levels of lead in some soil samples indicate a potential risk of health effects for young children in Copper Cliff, Coniston, Falconbridge and Sudbury Centre."

Plate 2: Sources of Oral/Dermal Lead Exposure to Toddlers in the Sudbury Centre



Market basket contribution (Supermarket food) is the largest contributor to lead exposure in toddlers. Household dust is generally the second largest contributor to lead exposure (15% to 19%). Some of the lead in household dust may come from outdoor soil, which in turn may be impacted by metal production emissions. However, lead levels can be elevated in household dust from historic use of lead-based paints and other consumer products such as window blinds, gasoline and many other products (SARA Group, 2001)

Lead poisoning can, in some cases, be traced to a specific route or source of exposure based on the individuals blood lead isotope ratio. It was considered that lead isotope ratios did not change during physical, chemical or biological processes. Thus, lead isotope ratios have been used as fingerprints to identify possible lead sources.

The objective of this study was to evaluate the application of using Pb isotopes for differentiation of contaminant source areas in northern Ontario in diverse environmental media, namely precipitation and vegetative species which absorb nutrients primarily from precipitation.

In order to determine the point source Pb contributors of anthropogenic pollution within northern Ontario an evaluation of the greater area and point source areas was conducted.

2.0 Background of Pb Origins in Northern Ontario

Northern Ontario, a region of the Canadian Shield north of Lake Huron, has an economy thriving off mining, forestry and hydroelectricity generation. Residents endure cold winters from November through March and warm summers during the months of June, July and August. The prevailing wind direction within the northern Ontario area normally follows a south-west transect, with some seasonal patterns being observed (Consulting P. A., 2004). For example, during the summer months the winds are typically from the southwest, south and west (Consulting P. A., 2004). During the colder winter seasons, the winds are usually blowing from the northwest to north (Consulting P. A., 2004). Wind direction is one of the more important meteorological conditions determining both the fate and the origin of aeolian aerosolic of the lead particles. In the map of Ontario in Plate 3, the two transect lines illustrate the particular area of northern Ontario under study.

Plate 3. Map of northern Ontario showing the two main study area transects from Timmins to Sudbury and Sudbury to Sault Ste. Marie, Ontario

The region traversed by the two transects provided exposure to airborne emissions of the five most important emitters of atmospheric lead pollution in Northern Ontario, thus allowing for indirect contaminant monitoring. Lead, an element with a series of stable isotopes whose relative abundances may be characteristic of diverse material sources, was chosen as the element of interest because the four largest point sources of atmospheric metal pollution in northern Ontario all contain Pb in their ores. The major point source potential emitters of lead to the atmosphere in soluble or aerosolic particle form examined in this study are listed as follows

1. Xstrata Falconbridge - Kidd metallurgical Site Timmins Operations
2. Vale Inco - Copper Cliff Smelter Complex
3. Xstrata Falconbridge - Sudbury Nickel Smelter Complex
4. Essar Steel Algoma - Steelworks

A summary of the four major point sources can be seen in Table 4 with air emission data reported from the 2009 National Pollution Release Inventory:

Table 4. Major Point Source Pb Emissions Origins and Contribution in northern Ontario (Canada, 2009)

Company	Division	Ore Type	2004 Pb Air Emissions (kg)	2009 Pb Air Emissions (kg)
Xstrata Canada Corporation-Copper Division	Kidd Metallurgical Site-Timmins	Cu Zn PGE	$4.5x10^3$	$2.3x10^4$
Vale Inco	Copper Cliff Smelter Complex	Ni-Cu-PGE Sulphide Ores	$5.5x10^4$	$8.1x10^3$
Xstrata Canada Corporation	Sudbury Nickel Smelter Complex	Ni-Cu-PGE Sulphide ores	$7.7x10^3$	$5.1x10^3$
Essar Steel Algoma	Steelworks Sault Ste. Marie	Iron Ore	N/A	194

2.1 Regional Profiles

2.1.1 Greater Sudbury Region

Lead containing ores smelted in Xstrata Falconbridge and Vale Inco Sudbury smelting operations originate primarily from a major geological structure from the second largest known crater on the planet. This oval shaped "mineral-rich basket" containing nickel and other metals spans a 60 km by 27 km area (Laurentian, 2003). Lead is locally enriched in Sudbury ores, occurring in galena and various selenide and telluride minerals associated with chalcopyrite and sphalerite (Ames, Kjarsgaard, & Douglas, 2007). The discovery of the metal-rich ores of the Sudbury basin encouraged the change from a railway junction on the TransCanada Rail to a mining and smelting focused community because of the global interest in the secure source of valuable minerals located in this crater. Sudbury became home to one of the largest nickel mining complexes in the world. As Sudbury's Nickel production boomed after World War II, the waste sulphur oxide gases caused severe ecological damage in the area, the most recognizable being the almost total destruction of vegetation in the region. This impact led to a reputation as being one of the most unattractive urban places in Canada. Atmospheric lead emissions from the regional smelters are produced by the smelting and refining of platinum group metals (PGM'S) from the regional ores. Specifically, the Sudbury Basin Ni-Cu-PGE and hydrothermal Zn-Pb-Cu deposits which contain trace levels of key elements such as S, Se, Te, As, Sb, Te, As, Sb, Bi, Sn, Hg and of course Pb (Cabri, 1981). Concerns for the ecological and biological effects of this air pollution, coupled with the changing regulations for acceptable SO_x levels near surface, led to the construction in 1972 of the 381m super stack at the Vale smelting operation. The Copper Cliff Vale smelter complex has two principal chimneys, one standing at 381m and the other at 194m. The Xstrata Falconbridge smelter has one operational stack emitting gases and aerosols at 94m. Other lead emissions from the smelter complexes also originate from sources at lower levels such as roof vents and a pelletizer plant which has two 45m stacks (Walter, 1985). The construction of the 381m freestanding chimney was designed to disperse sulphur gases and

other metal containing particulate by-products (including lead) from the smelting operation away from the city. Although emissions were reduced locally, a large number of acid lakes were created with high metal contaminant loadings in the areas downwind of the smelter complexes (Potvin & Negusanti, 1995). This ecological impact gave rise to an action plan starting in the 1990's to reduce gaseous emissions from the super stack by approximately 90%, with a contaminant reduction in fine metal-rich aerosolic materials. The reduction in total metal-rich aerosolic materials was also in the 90% range, with elemental reductions for metals such as lead being measured at a similar level. (Ontario, 1994)

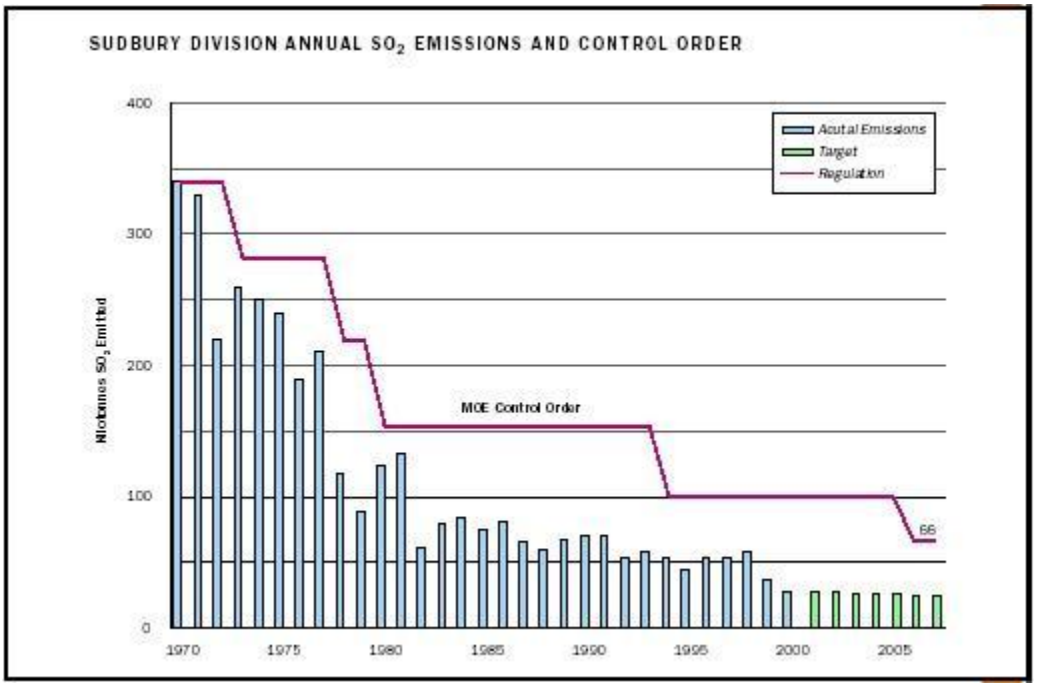


Figure 1. The decline of SO2 Emissions in Sudbury Ontario from 1970-2005 (Air Quality Trends City of Greater Sudbury, Ontario 1953-2002, 2004)

With the completion of the initial emission reduction project in 1994, ongoing studies have documented a steady decline in total emissions. Now Sudbury has acquired a more flattering reputation, being recognized internationally for the successes of the ecological

recovery, no longer with a landscape comparable to the moon's surface but one similar to the picturesque regional landscape with its original northern beauty.

2.1.2 Timmins Region

The Xstrata metallurgical plant located in Timmins Ontario is another source of atmospheric lead emissions in the northern Ontario regions. The plant began operation in 1966, producing copper, zinc, indium, cadmium, silver and sulphuric acid. The metals are mined from one of the largest and richest volcanogenic massive sulphide deposits in the world (Xstrata, 2011). The Kidd Creek metallurgical facility consists of a copper concentrator, smelter, refinery, and a zinc, cadmium, indium and sulphuric acid plant. The facility obtains the bulk the of the feedstock from Glencore Kidd Creek Mine, which is currently the deepest base metal mine in the world. Xstrata (now Glencore) announced its decision in 2009 to permanently cease operations at its Kidd Metallurgical facilities in June 2010 (Xstrata, 2011). The Kidd mine produces annually around 45,000 tonnes of copper and 130,000 tonnes of zinc contained in concentrates (Xstrata, 2011), which will, in future, be processed at the Glencore Facilities in Rouyn-Noranda, PQ.

2.1.3 Sault Ste. Marie Region

Approximately 300km due west of the Sudbury smelting complexes is the Essar Steel Algoma industrial complex in Sault Ste. Marie, Ontario that also contributes to the Pb anthropogenic emission load of the region, but to a lesser (although significant) extent. Algoma currently is the third largest steel producer in Canada, having been in operation for over 100 years with the capacity to produce over 2.8 million tonnes of steel per year. The Algoma complex mainly produces steel strip (i.e. plate and sheet type), as well as having blanketing operations and a production of welded beams. The Algoma products are marketed within

Canada, the United States, and internationally. The primary steel making facilities include two blast furnaces, three coke batteries, two 260 short ton basic oxygen furnaces, with two ladle metallurgy stations for refining and alloying. Gaseous emissions and metal aerosols are the most prominent sources of waste from electric arc furnaces (Essar Steel, 2011).

Essar Steel Algoma has completed many initiatives to minimize air pollution, having recently installed an oven pressure control system on a coke battery to achieve 70% reduction in coke oven emissions. The company installed bag house technologies on their blast exhaust systems to capture air particulates to minimize point source emissions. The company is involved in many ongoing initiatives to minimize particulate emissions from material including coal dust, where there has been a fugitive emission reduction of by 50% following the application of dust suppressants. Essar Steel has an air quality monitoring program which monitors total reduced sulphur and PM10 (fine suspended particulates less than 10 microns in diameter) through two ambient air quality monitoring stations located within the community (Essar Steel, 2011).

Identifying the major sources of Pb contamination in northern Ontario is crucial in determining the fate of Pb in environmental media collected throughout northern Ontario. Point sources and environmental media Pb contaminants can be traced using isotopic ratios, lead in the case of the study. The use of isotopic ratios to fingerprint anthropogenic pollution sources is based on many principles and an understanding of how to use them.

3.0 Project Background

3.1 Isotope Ratio Principles for Lead as a Tracer

The global average natural isotopic abundances for lead are shown in (Table 5). However, the rise in global anthropogenic emissions since the industrial revolution has led to a shift in the natural abundances of the ratios of these isotopes of lead in many environmental media.

Table 5. Natural Average of Pb Isotopes in Earth Surface Media (Education, 2013)

Isotopes of the Element Lead with a Known Natural Abundance		
Mass Number	**Natural Abundance**	**Half Life**
204	1.40%	$\geq 1.4 \times 10^{17}$ years
206	24.10%	Stable
207	22.10%	Stable
208	52.40%	Stable

Although the sources of Pb and relative contribution from each different source cannot be traced from the total concentrations as measured in environmental media (air, water, and soil), the varying ratios in lead isotopic abundances in samples from the different sources can potentially provide an effective method for monitoring long range atmospheric transport of anthropogenic pollution. The inability to accurately predict the contaminant source (e.g lead) from concentrations alone often puts the cleanup liability under dispute, slowing down the remediation process (Morrison, 2000). Furthermore, following the misassignment of contaminant source, the true Pb source may continue to emit and contaminate the environment if pollution is attributed to an incorrect source. An isotopic composition of an element is also called the signature or fingerprint. The isotopic signature of an element is simply the ratio of the abundance of one isotope over another is a specific sample. An isotopic signature of a sample thus provides

a means of tracing origins of the contaminant element in that particular sample. The measurement of isotopic abundance of an element such as lead is superior to using concentrations alone in tracing pollution sources because isotope ratios are significantly more sensitive tracers (Hefa & Yuanan, 2010).

3.2 Principles of Pb Isotopic Fingerprinting

Isotopic fingerprinting of lead (Pb) may be used as a tool to trace the origins of anthropogenic pollutions of diverse terrestrial media using the following data interpretation approaches.

3.2.1 Naturally Occurring Lead

There are four naturally occurring stable isotopes of lead, namely 204, 206, 207, and 208. This large number of stable isotopes provides many possible variations in isotope ratios such as Pb^{208}/Pb^{204}, Pb^{206}/Pb^{204}, Pb^{207}/Pb^{206}, which may be used as environmental forensic tools. With the exception of primordial ^{204}Pb, the relative abundance of each Pb Isotope is dependent on the radioactive decay ^{238}U ^{235}U and ^{232}Th to ^{206}Pb, ^{207}Pb and ^{208}Pb respectively over geological time (Faure, 1986). The decay processes ^{238}U, ^{235}U are shown in Plate 4, with Plate 5 showing the decay process of ^{232}Th.

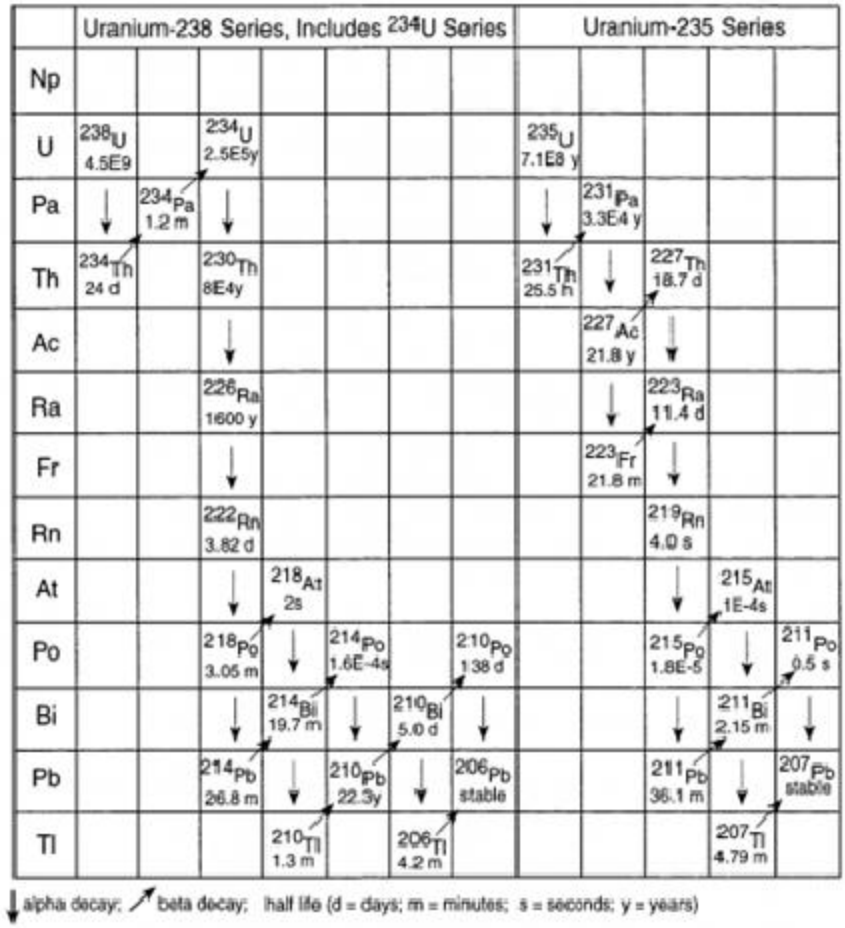


Plate 4. Decay process of Uranium 238 and 235

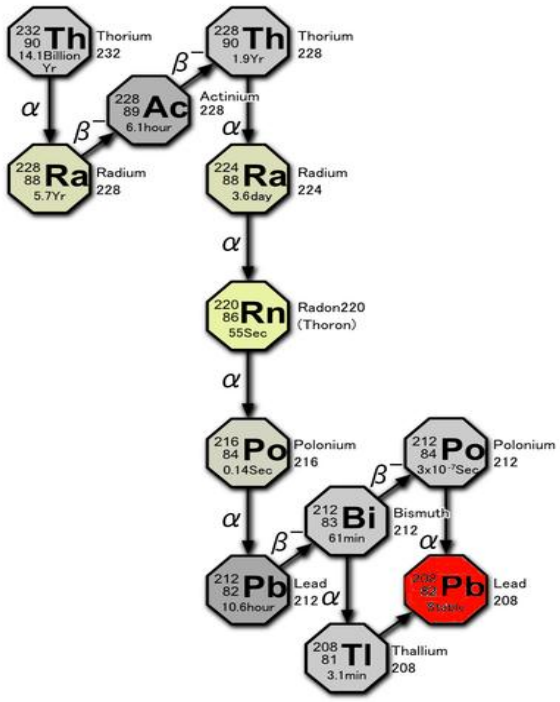


Plate 5. Radioactive decay of ^{232}Th

The major point source anthropogenic Pb emitters in Northern Ontario have different ore bodies being mined from different geological formations to supply concentrate to the smelting and refining processes. The abundances of the Pb isotopes in the ore bodies varies depending on the geological time period in which the geological formations were formed. Thus, the Pb isotopic abundances characteristic of different Pb containing minerals are a product of numerous geochemical processes including radioactive decay of U and Th to Pb, the relative proportion of U, Th and Pb in the system, and actual mixing of Pb from different sources. (Chang & Yu, 2009)

3.2.2 Distinct Isotope Signatures

The individual Pb isotopic ratios found in natural materials range from 14-30 for ^{206}Pb/^{207}Pb, 15-17 for ^{107}Pb/^{204}Pb, and 35-50 for ^{208}Pb/^{204}Pb, with values outside these ranges being not uncommon (Doe, 1970). The many different ores throughout northern Ontario and neighboring

jurisdictions have their own distinct isotopic signature. The large ranges in isotopic ratios observed stems from the fact that Pb is the daughter product from a decay chain whose initial elements (U and Th) have different geochemical behaviors, with the isotopic signature each distinct ore being made up of Pb isotopes from the independent decay chains (Chang & Yu, 2009).

3.2.3 Isotope Fractionation

The Pb isotopic composition of individual minerals or of an ore body or anthropogenic source does not change during processing or the transition to a secondary weathering environment unless there is mixing with secondary Pb sources. Apparent Pb isotope fractionation can only occur over geological time as a consequence of parent isotope disequilibrium between Th and U, rather than daughter Pb Isotope fractionation (Neymark & Amelin, 2008). As a result, Pb isotope ratios only vary according to their geological sources, and the isotopic compositions measured in the samples reflect those of the Pb sources or results of mixing, if multiple Pb sources exist. For example, if the ore mined from the Stobie Mine had a $^{208}Pb/^{204}Pb$ isotopic signature of 14.57 then the isotope ratios will be identical in aerosol and dusts emitted from the processing of that post smelting process. Thus, any measured change in isotopic abundance for Pb emitted to the environment during the smelting process could only change because of blending or mixing with ores from other ore bodies during the grinding and preconcentration process of the milling operations with ores of higher or lower isotopic signatures.

Local Sudbury Study of SO_2

In an analysis of the smelter plume sulphurous gases from Sudbury Ontario, Nriagu and Coker (Nrigu & Coker, 1978), suggested that the sulphur isotopic composition in emitted SO_2, SO_3,

(and the acids formed with water vapor) did not differ from that measured in source sulphide minerals by more than two to three permil ‰. This study, along with many others globally imply that emission sources generally transfer the sulphur isotopic signature of the process feedstock to the gaseous compounds released to the atmosphere by the chemical, combustion or metallurgical processes active. The study by Cortecci and Longinellis (Cortecci & Longinellis, 1970) took samples of SO_2 in the smelter stack and plumes from the former Vale Inco and demonstrated a constancy of sulphur isotope ratio values over both days and between years, which suggested a long-term similarity revealing that the variability of sulphur isotope ratios in the ore feeds between years is relatively small. In the receiving environment, environmental media such as precipitation and growing vegetation will inevitably be exposed to the emissions irrespective of the isotopic signatures. The vegetation will absorb in the transpiration stream dissolved elements, and will have minimal fractionation effects on dissolved heavy isotopes for elements such as lead. Thus, wet deposition samples will contain the mixed isotope ratios of all different sources of sulfur and metal contaminants from atmospheric pollution upwind from the collection site. Further, vegetation such as lichens which primarily obtain their nutrients from precipitation will contain the isotopes of elements such as sulphur or in the case of this thesis lead, in ratios reflecting those on the impinging precipitation. These studies suggest that, Sudbury may be an excellent area for studying the direct uptake and impacts of atmospheric deposition from its emissions in aquatic media and biota because of long-term constancy of isotopic signatures suitable for use as tracers, However, aside from the aforementioned movement of other key elements in emissions using specific isotopic abundance data potentially characteristic of regional industrial complexes.

3.3 Source Apportionment

In this study mixed isotope ratio samples are collected from the wet deposition and lichen samples to produce an isotopic fingerprint of different point sources in northern Ontario. Determination of isotopic ratio compositions leads to contributions from the different major sources using bivarant mapping techniques (the analysis of two variables (often denoted as *X*, *Y*), for the purpose of determining the empirical relationship between them) along with meteorological data. These mapping techniques involve plotting known Pb isotope ratio values from point source emitters. Once isotope ratio data is gathered, Pb isotope ratio values are obtained from the mixed isotope samples (wet deposition and moss) and are then plotted. Patterns arise in mapping and observable mixing lines occur between point sources. The location of the mixed sample with respect to the mixing arrays gives an indication of the apportionment of pollution in that sample. Since numerous potential sources exist, it is vital to be able to distinguish them from each other in a given area in order to assess their relative impacts. The Pb isotopic compositions in Pb containing ores depends only on the source ores; ores from different part of the world often have their own Pb isotopic signatures which are preserved during transport over vast distances and transfer processes. Therefore, from the ratios of the isotope concentrations of ^{208}Pb ^{207}Pb and ^{206}Pb detected in a sample it is possible to pinpoint the source of Pb by matching the Pb isotopic composition found at the contamination site with those of the potential sources. It is also possible to apportion the contribution of the major sources based on their Pb isotopic compositions in cases where lead pollution resulted from multiple sources. The isotopic compositions of different potential Pb sources obtained from direct measurements and literature can be plotted on a diagram using two of the isotope ratios 206, 207 and 208, eg. 206/207 is commonly used in environmental studies while 207/206 is commonly used in geochronology studies. By mapping the Pb isotopic compositions of the samples from the

contaminated site, the major sources of the Pb can be identified based on the resemblance of isotopic fingerprints.

4.0 Tracing Lead in Snowpack

4.1 Introduction

Variations in the chemical composition of snowfall reflect chemical differences of aerosols transported from source areas by air masses from which they are derived. The isotopic compositions of snowpack samples should thus represent a "naturally" weighted sample of the wet and dry deposition over the deposition period. There are several advantages of collecting snowpack over rainwater. For example, the metal content within snowpack represents the fallout accumulation over the whole snowing season. The snow crystal, because of bigger specific area, tends to be more efficient in capturing particles from the atmosphere. Snow was collected during the month of January indicating the average atmospheric pollution in the early winter season from the initiation of permanent snow cover for the season. The prevailing wind direction within the Sudbury area normally follows a south-west to north-east transect, however, seasonal patterns can be observed (Potvin, 1976), with winds usually blowing from the northwest to north during the colder winter season (Potvin, 1976). The wind direction is an important meteorological condition for the determination of the origin of elements such as lead (Alian, 1980).

4.2 Methodology

Snowpack samples were collected during the winter month of January 2010, from the 15^{th} to the 20^{th}. Snowpack was collected along two main transects; an East -West transect from

Sudbury to Sault Ste. Marie, and a South- North transect from Sudbury up through Timmins to Kapuskasing, Ontario. These transects also correspond with transects used in the moss sampling procedure in future discussion. Multiple samples were taken at a 20km radius around each point source listed in Table 4, wherever availability allowed.

Plate 6. Snowpack sample Collection location Timmins Metallurgical site

All samples except those sampled around each point source were retrieved kilometers away from cities, industries, highways, main roads, and railways to obtain a regional atmospheric signal rather than that of a local point source. A strict set of criteria were used in the selection of the sampling sites, which included sampling in uninhabited areas at least 1 km away from villages, summer resorts, and secondary roads. In most cases, the immediate sampling site was reached on snow shoes. Most samples were obtained in "clear" areas of the snowpack so as

to reduce the contribution from any overlying vegetation canopy. Nevertheless, the samples occasionally contained millimeter sized vegetation debris, such as fragments of spruce/fir needles, deciduous tree leaves, or bark. This local vegetation material would have been a consequence of wind activity during or between the snowfall events. The sampling date, location, GPS coordinates, openness of site, pictures and additional notes were recorded for each sample collected.

The snowpack reflect the integrated atmospheric signal for the early part of the winter season. The snowpack was sampled using a plastic shovel that was covered with a clean polyethylene bag which was removed and replaced between the sampling of each snowpack (Plate 9). The snow sample was stored in a double bagged polyethylene bag in pails for transport to the laboratory. All samples were collected with clean latex gloves.

Plate 7. Snowpack sample collection showing double bagged polyethylene bag containing approximately 3L of snow.

The snowpack samples were melted within hours of collection, with the melt waters being collected and stored in pre cleaned polyethylene bottles. The bottles were cleaned three times using 5% ultra pure nitric acid followed by three rinses with ultra pure water. Each sample yielded approximately 3L of melt water. The samples were filtered through a pre cleaned 0.45 micrometer cellulose acetate filter into a pre cleaned Nalgene filtration apparatus equipped with Teflon tubing. The cleaning procedure for the acetate cellulose filters and Teflon tubing involved filtering approximately 1L of nanopure water prior to sample processing. The Nalgene filter apparatus was pre cleaned by washing three times with 2% nitric acid and rinsing three times with ultra pure water. The pH of each sample was recorded, with all samples being acidified with ultrapure HNO_3 to a pH of 2 ± 0.2. The samples were stored at approximately 4°C until analysis. The lead isotopic abundance of the samples was determined by ICP-MS in the Geochemistry Laboratory of the Minerals Exploration Research Centre.

Each sample was analyzed 10 times with SRM 981 and 982 which was analyzed for mass bias correction and quality control purposes. Details of the quadrupole ICP MS Pb isotope analysis at Laurentian University are explained in (Ulrich, 2010). The average standard deviation and percent relative standard deviation of the combination of all snowpack samples is shown in table 6. Table 7 shows the standard deviation and the relative standard deviation of NIST SRM 982 that was used as an external reference material.

Table 6: Average Standard Deviation and Percent Relative Standard Deviation of all Snowpack Samples

Isotope Ratio	^{207}Pb / ^{206}Pb	^{208}Pb / ^{206}Pb	^{206}Pb / ^{204}Pb	^{207}Pb / ^{204}Pb	^{208}Pb / ^{204}Pb
Standard Deviation	0.0049	0.0113	0.2069	0.1825	0.4323
Std Dev Range	0.0013-0.014	0.0038-0.0290	0.0469-0.5550	0.0529-0.4738	0.1058-0.9907
%RSD	0.5617	0.5337	1.1401	1.1596	1.1303
%RSD Range	0.1505-1.679	0.1658-0.86758	0.2920-2.989	0.3440-3.024	0.2780-2.582

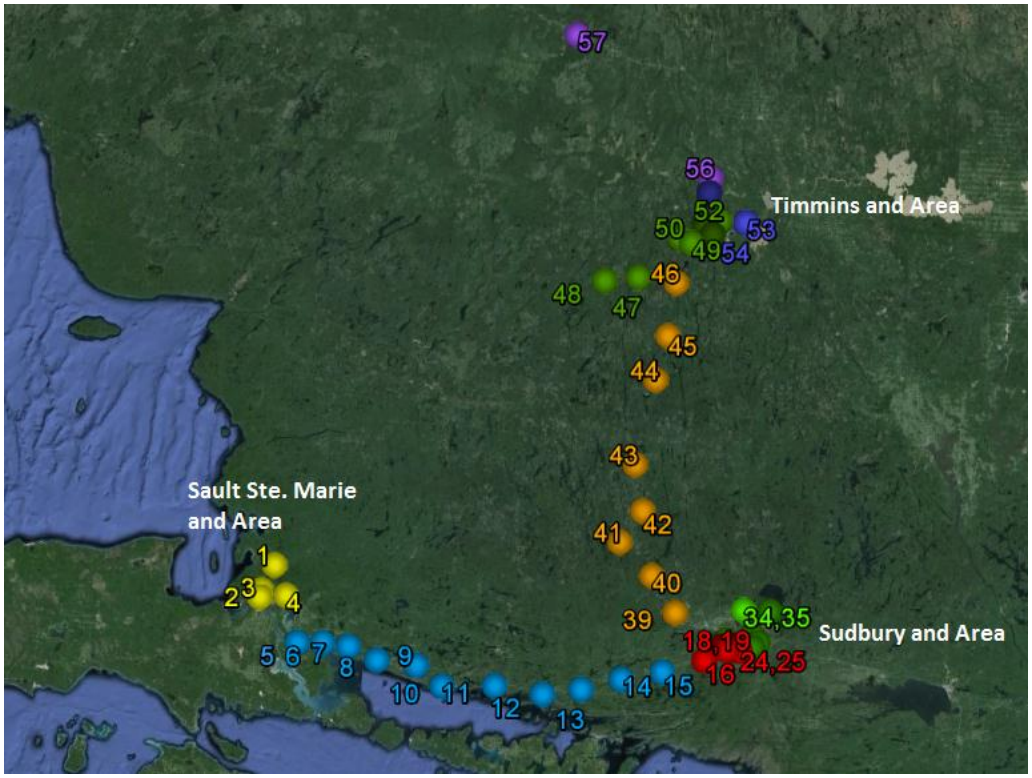
Table 7: Standard Deviation and Relative Standard Deviation of NBS 982 Used as an External Quality Control Check

NBS 982	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$
average	0.46695	1.00005	36.727
stdev	0.00025	0.00081	0.057
rsd	0.054	0.081	0.155

4.3 Results

Lead isotopic compositions are presented from snowpack samples retrieved from 57 sites along the W-E Transect and the N-S Transect. Sample collection along these two transects was conducted in January during the 2010 shutdown of the Vale Copper Cliff smelter complex. This complex was temporarily shut down due to the maintenance and production workers going on strike. A map of these two transects can be seen in Plate 10. The numbers correspond to snowpack sample collection number. All sample data for the snowpack is located in Appendix A. The quality control standard that was used was NBS 982, these results can also be found in appendix B.

Plate 8. West East Snowpack Transect between Sault Ste. Marie and Sudbury and South North transect from Sudbury up through Timmins to Kapuskasing



Of importance, the area covered by both transects provided indirect monitoring of the five most important emitters of atmospheric lead contamination in northern Ontario. Some of the major emitters are listed in table 6 as reported by the Ministry of the Environment.

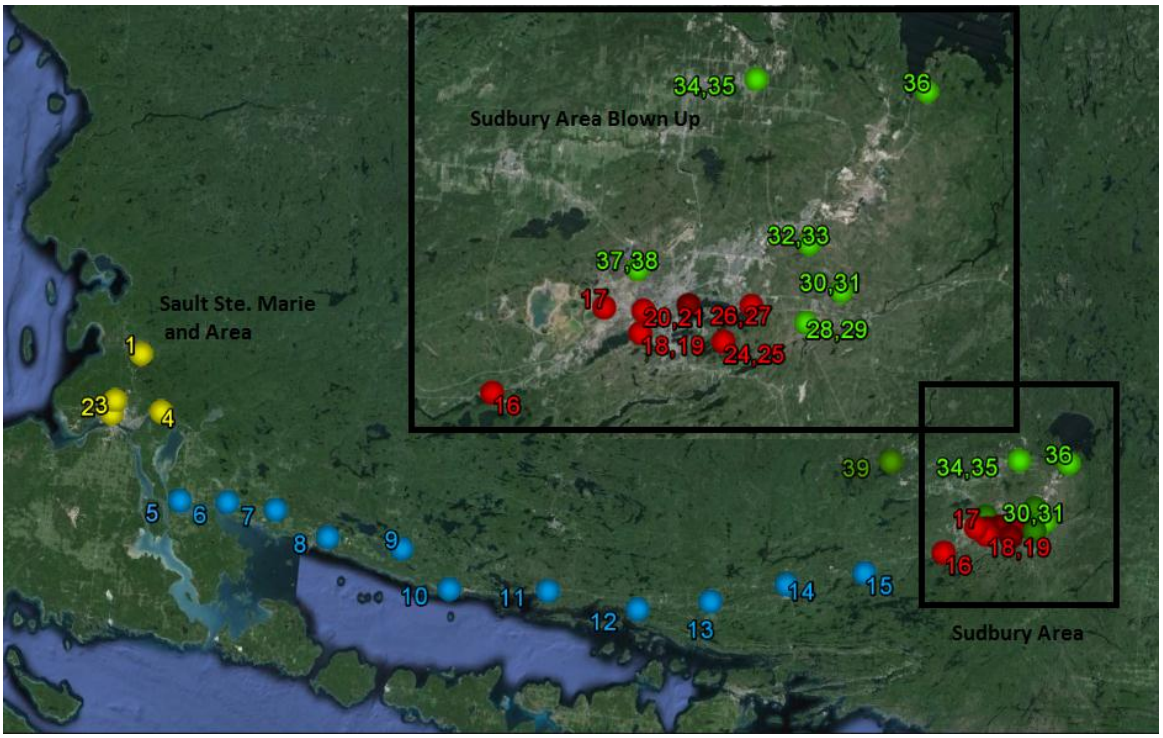
Table 8. The Five Largest Atmospheric Lead Polluters in Northern Ontario

Company	Location	Kg of Lead
Xstrata Canada Kidd Met Site	Timmins	23058
Vale Inco Smelter Complex	Copper Cliff	8083
Xstrata Canada Nickel Smelter	Falconbridge	5074
Vale Inco Copper Cliff Refinery	Copper Cliff	1700
Algoma Steel	Sault Ste. Marie	196

4.3.1 W-E Transect Results

The following reports results from the West to East Transect between Sudbury and Sault Ste. Marie. This transect is shown in plate 11 with sample numbers corresponding to sample collection number.

Plate 9. West East Transect between Sault Ste. Marie and Sudbury



In the following figure the isotope ratios of Pb^{208}/Pb^{204} and Pb^{208}/Pb^{206} were plotted from direct measurement of snowpack samples retrieved from different locations along the W-E transect between Sault Ste. Marie and Sudbury, Ontario. The plotting of multiple isotope ratios provides a three way mixing plot which enables the determination of any other potential sources that could be possible lead contributors to the collected snowpack. The colors in figure 2 correlate with the sampling areas on plate 11.

Figure 2. Snowpack Mixing Graph of Pb^{208}/Pb^{206} vs. Pb^{208}/Pb^{204} along the W-E Transect During the Vale Inco Copper Cliff Smelter Shutdown

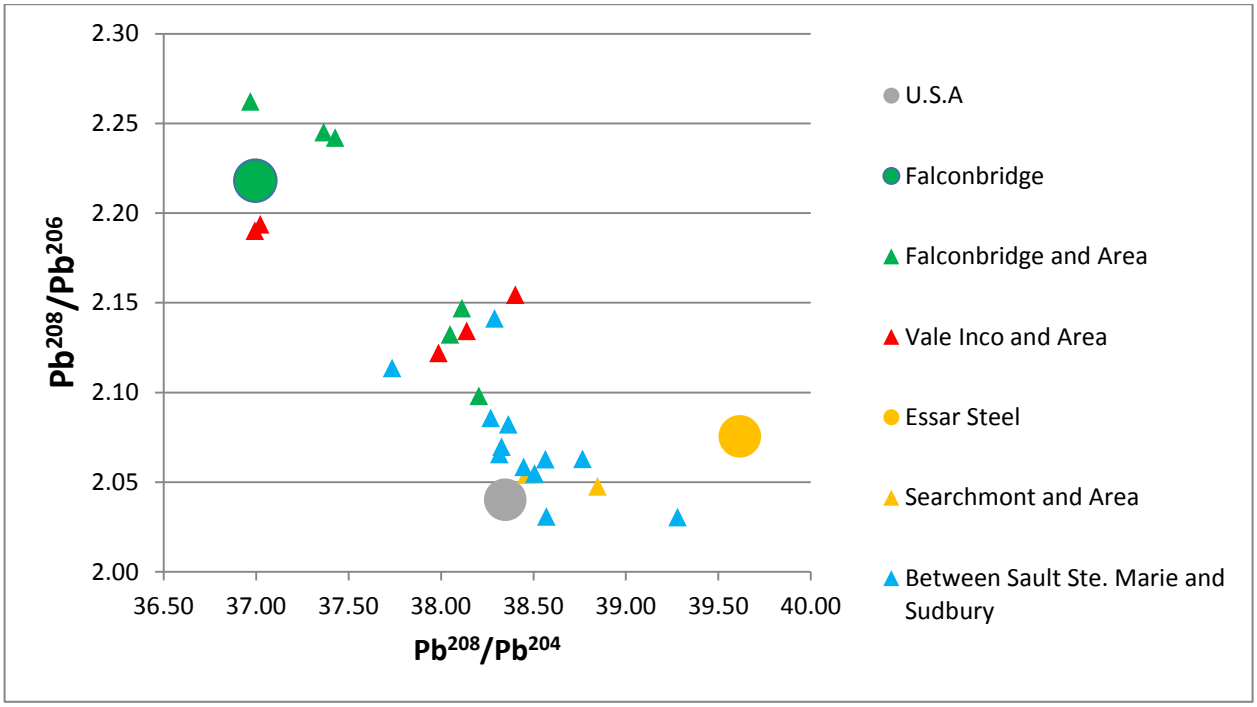


Table 9. Sample data from snowpack along the W-E transect during the Vale Inco Copper Cliff Smelter Shutdown (Figure 2 Data)

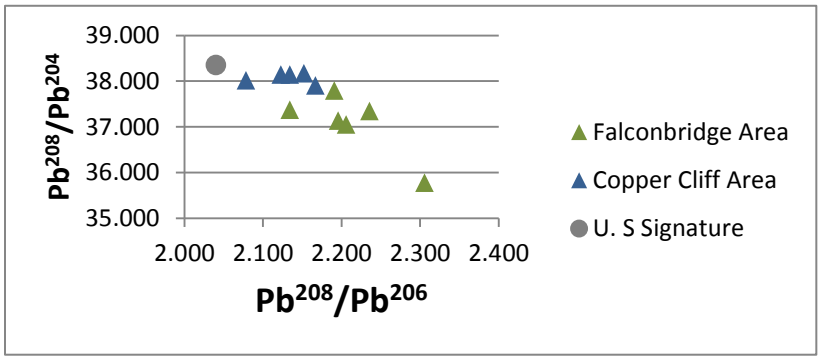
Sample ID	Location	Lat	Long	Pb208/Pb206	Pb208/Pb204
Point Source Data					
3	Essar Steel Sault Ste. Marie	46°31'56.34"N	84°21'59.21"W	2.08	39.62
36	Falconbridge Smelter	46°30'12.33"N	80°49'7.54"W	2.22	37.00
	USA			2.04	38.35
Individual Sample Data					
1	Searchmont, Sault Ste. Marie	46°41'45.96"N	84°16'57.73"W	2.05	38.85
2	Peoples St. Sault Ste. Marie	46°34'4.52"N	84°21'34.64"W	2.05	38.51
4	East of Sault Ste. Marie	46°31'56.34"N	84°21'59.21"W	2.05	38.46
5	Browns Island	46°33'13.20"N	84°10'46.62"W	2.06	38.77
6	Off Bear St, Portlock	46°19'49.35"N	84° 4'4.64"W	2.05	38.51
7	Lafarge, Bruce Mines	46°20'27.45"N	83°53'16.91"W	2.11	37.74
8	Walford, Thessalon	46°20'11.78"N	83°42'12.38"W	2.08	38.36
9	James St, Iron Bridge	46°16'54.27"N	83°29'43.12"W	2.06	38.45
10	Carmeuse Lime, Blind River	46°16'28.08"N	83°12'51.58"W	2.03	39.28
11	Spragge	46°11'0.56"N	83° 1'14.15"W	2.03	38.57

12	Spanish River	46°12'24.14"N	82°39'7.98"W	2.07	38.32
13	Massey	46°11'1.19"N	82°18'40.52"W	2.07	38.33
14	Domtar Pulp and Paper, Espanola	46°13'16.92"N	82° 2'35.57"W	2.06	38.57
15	Beaver Lake	46°17'2.60"N	81°45'53.09"W	2.09	38.27
16	Penguin Research, Naughton	46°19'53.71"N	81°28'41.16"W	2.14	38.29
17	Vale Inco, Copper Cliff	46°24'6.84"N	81°11'18.58"W	2.13	38.14
18	Kelly Lake, South End Sudbury (1)	46°28'26.82"N	81° 4'32.03"W	2.12	37.99
21	Big Nickel, Sudbury(1)	46°27'27.64"N	81° 2'0.03"W	2.15	38.40
25	Laurentian conservation, Sudbury(1)	46°28'29.27"N	81° 1'56.55"W	2.19	36.99
26	Minnow Lake, Sudbury (1)	46°27'26.14"N	80°56'30.55"W	2.19	37.02
28	Vale Inco, Coniston (1)	46°29'9.82"N	80°54'54.46"W	2.24	37.43
30	Xstrata Falconbridge (1)	46°30'12.33"N	80°49'7.54"W	2.22	37.00
32	Make Rd, Garson (1)	46°32'11.50"N	80°51'31.77"W	2.26	36.97
35	Hanmer (1)	46°39'23.29"N	80°56'0.56"W	2.13	38.05
36	Skead	46°39'33.84"N	80°44'44.36"W	2.25	37.37
37	Clarabelle/Lasalle Sudbury (1)	46°30'19.30"N	81° 2'35.40"W	2.15	38.11
39	Onaping	46°37'31.18"N	81°25'2.25"W	2.10	38.21

208Pb/ 206Pb and 208Pb/ 207Pb values of 2.055 + .019 and 2.470 +

The isotope ratios of samples collected around the Vale Smelter, and samples collected around Falconbridge, Xstrata Smelter are displayed in figure 3. All sampling was done when the Vale smelter was in operation. The following graph depicts the small differences in isotope ratios in samples from the two locations with respect to the U.S fingerprint.

Figure 3. Pb^{208}/Pb^{204} vs Pb^{208}/Pb^{206}. Samples Collected around the Vale Inco Smelter and Falconbridge Xstrata Smelter during Vale Inco Smelter Operation



Snowpack samples were collected both during the shutdown period and again after the Copper Cliff smelter started back up. The following graphs illustrate the isotope ratios in snowpack from both the Copper Cliff and Falconbridge areas before and after the shutdown.

Figure 4. Pb^{208}/Pb^{206} vs. Pb^{208}/Pb^{204} of the Copper Cliff Area before and After the Shutdown of the Vale Inco Smelter Complex

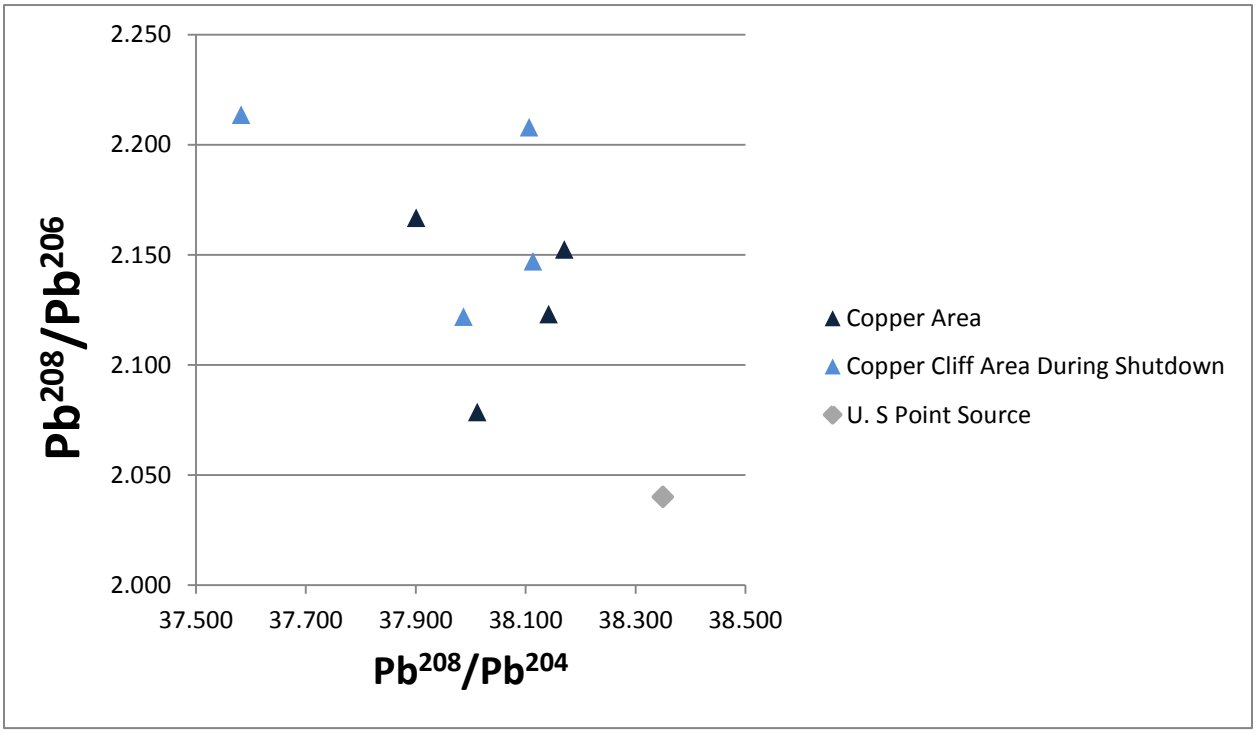


Figure 5. Pb^{208}/Pb^{206} vs Pb^{208}/Pb^{204} of the Falconbridge Area Before and After the Shutdown of the Vale Inco Smelter

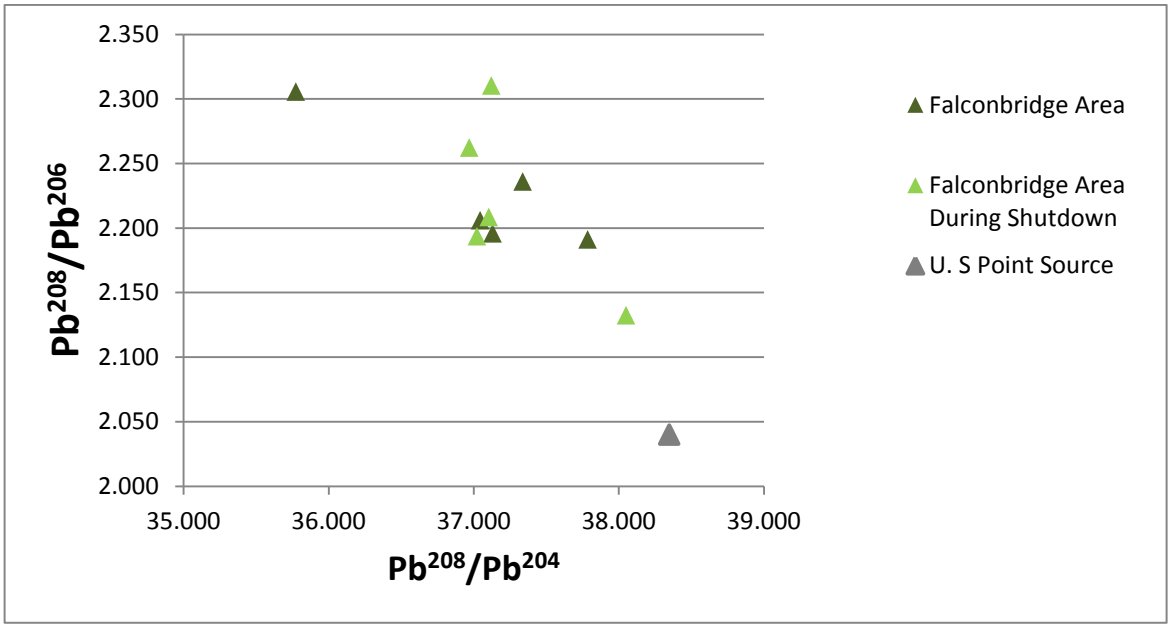


Table 10. Sample data from snowpack in the Sudbury, Greater Sudbury region before and after the Copper Cliff Smelter Shutdown.

	Before the Shutdown		During the Shutdown	
Falconbridge Area	Pb208/Pb204	Pb208/Pb206	Pb208/Pb204	Pb208/Pb206
Minnow Lake, Sudbury	37.787	2.191	37.023	2.194
Vale Inco, Coniston	37.339	2.236	37.106	2.209
Xstrata Falconbridge	37.045	2.206	37.122	2.310
Make Rd, Garson	35.775	2.306	36.971	2.262
Hanmer	37.132	2.196	38.051	2.132
Skead	37.367	2.134		
Copper Cliff Area				
Kelly Lake, South End Sudbury	38.171	2.152	37.987	2.122
Big Nickel, Sudbury	38.142	2.123	38.106	2.208
Laurentian conservation, Sudbury	38.012	2.079	37.582	2.214
Clarabelle/Lassalle Intersection Sudbury	37.901	2.167	38.113	2.147
Vale Inco, Copper Cliff	38.140	2.134		
U.S Signature	38.35	2.04		

4.3.2 S-N Transect Results

Snowpack samples were also collected along an S-N transect from Sudbury up through Timmins to Kapuskasing. Of importance, the major point source emitters along this transect are:

Falconbridge Xstrata's Smelter Operations (5074kg/yr Pb)

Timmins Xstrata Kidd Metallurgical Site (23058kg/yr Pb),

Note that the other major point source along this transect is the Vale Inco Smelter Complex in Copper Cliff was shut down during the sampling period. There are also some of the minor contributors to lead along this transect, with their respective annual emissions being:

Lake Shore Gold Corp Bell Creek Complex (13 kg/yr)

Goldcorp Canada Dome Mine (4.9kg/yr)

Xstrata Nickel Montcalm Mine (0.033kg/yr)

The following plate depicts the sampling area along this particular transect, with numbers corresponding to the specific sample sites. The numbers correspond to GPS locations and results that can be viewed in Appendix A along with QA/QC data in Appendix B.

Plate 10. North South Transect between Sudbury and Timmins

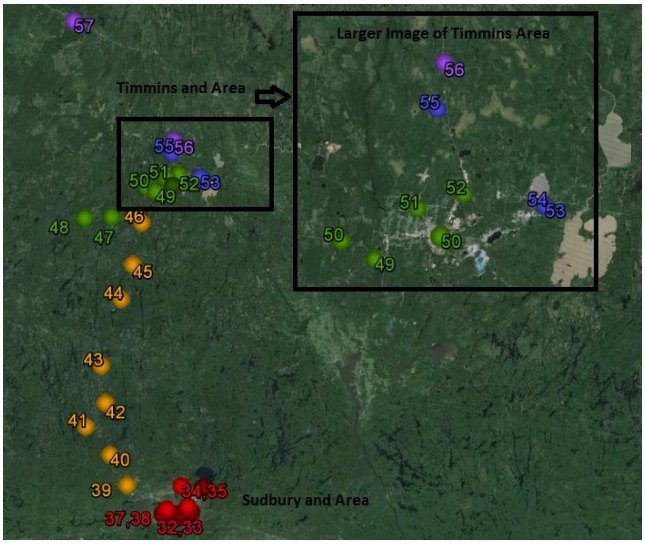


Figure 6 shows a three way distribution chart of Pb^{207}/Pb^{206} vs. Pb^{208}/Pb^{204} in snowpack along the S-N transect during the Vale Inco Shutdown. This transect represents a subset of samples at increasing distance north from the U.S border. Kapuskasing, located approximately two hours north of Timmins, was the furthest north of the sampling subsection.

Figure 6. South North Transect Snowpack Three Way Distribution during Vale Inco Smelter Shutdown Pb^{207}/Pb^{206} vs. Pb^{208}/Pb^{204}

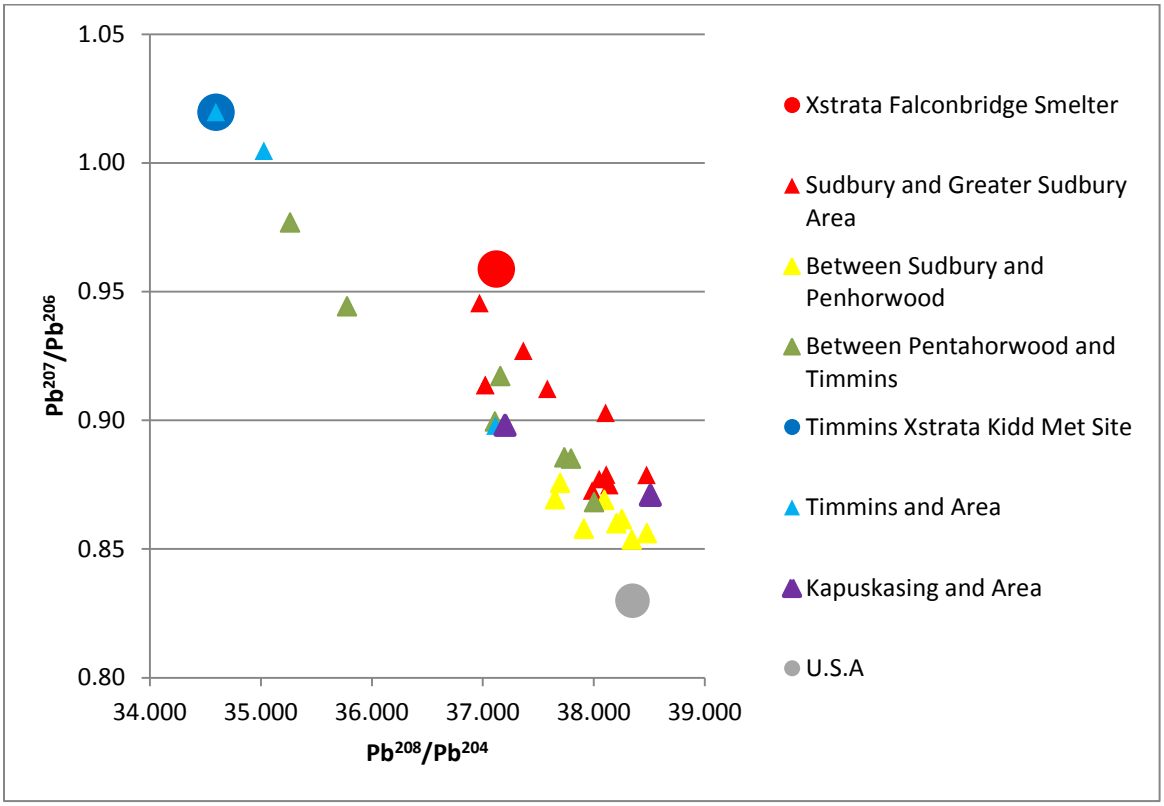


Table 11. Snowpack Pb isotope ratios for data collected along the S-N transect. Colors are coordinated with figure 6.

Sample ID	Location	Pb208/Pb204	Pb207/Pb206
17	Vale Inco, Copper Cliff	38.140	0.875
18	Kelly Lake, South End Sudbury	37.987	0.873
21	Big Nickel, Sudbury	38.106	0.903
23	Bell Park, Sudbury	38.475	0.879
25	Laurentian conservation, Sudbury	37.582	0.912
26	Minnow Lake, Sudbury	37.023	0.914
28	Vale Inco, Coniston	37.023	0.914
30	Xstrata Falconbridge	37.122	0.959
32	Make Rd, Garson	36.971	0.945
35	Hanmer	38.051	0.877
36	Skead	37.367	0.927
37	Clarabelle/Lasalle Intersection Sudbury	38.113	0.879
39	Onaping	38.206	0.860
40	Benny Lake	38.480	0.856
41	Gogama	37.652	0.869
42	Cutover	37.698	0.876
43	Big Truck	38.097	0.869
44	Kenetogami	38.344	0.854
45	Matagami Lk,	38.254	0.862
46	McKeowen	37.910	0.858
47	Halfway to Luzenac Pentahorwood	35.778	0.944
48	Luzenac Pentahorwood Point Source	38.004	0.868
49	Outside Montcalm Mine	37.111	0.899
50	Montcalm Rd.	37.734	0.886
50b	Luzenac Micronizing Plant	37.160	0.917
51	Xstrata Montcalm Mine	37.796	0.885
52	Big Water	35.265	0.977
53	Kidd Met Site Xstrata	34.596	1.020
54	Goldcorp Dome Site	37.114	0.898
55	Kidd Mine Site Xstrata	35.028	1.005
56	Black Pearl	37.202	0.898
57	Tembec Kapuskasing	38.512	0.871
	U.S Point Source	38.350	0.830

4.4 Discussion

4.4.1 W-E Transect Discussion

To determine the magnitude of impact each point source contribution to areas along this transect a three way graph (graph 2) was created using the isotope ratios Pb^{208}/Pb^{204} and Pb^{208}/Pb^{206}. These snowpack samples were all collected during the shutdown of the Vale Copper Cliff Smelter complex. Therefore, this point source smelter fingerprint should have little or no impact on the data set. The large dots in Figure 2 represent point source data from:

Essar Steel Algona (yellow)

Falconbridge Xstrata Sudbury Smelter Operations (green)

US coal fuel combustion (grey)

These three point sources each have their own distinct isotope signature, thus enabling the creation of a three way mixing chart. The other points that are plotted represent samples that were not collected in proximity to a point source, thus representing a mixing of ratios between point sources. The NPRI reported an annual release from Essar steel of 196kg, a relatively small amount when compared to the Xstrata Falconbridge total release of 5074kg/yr. Examination of emission release data in northern Ontario alone, suggests that the signatures of those samples collected between Sault Ste. Marie and Sudbury should mix with Xstrata Falconbridge more than Essar Steel, especially considering there is almost a 25 fold difference in Pb emissions. There was minimal mixing of Essar and Falconbridge when only these two point sources were graphed, this led to further investigation exploring the average isotope ratios from the coal fired power stations along the Ohio Valley and Midwestern states. The prevailing winds along this transect are from the South West with seasonal winter winds usually blowing from the northwest to north

(Potvin, 1976). Table 3 shows the massive amounts of Pb emissions from Coal Fuel Combustion sources in the Midwestern states.

Literature from previous studies ((Carignan j, 1995), show that this coal combustion has an average isotope ratio of 2.04, for Pb^{208}/Pb^{206} and 38.35, for Pb^{208}/Pb^{204} (Graph 1, grey circle). This source signature may explain the mixing of those samples collected between Sault Ste. Marie and Sudbury, Ontario. The samples in yellow represent those samples collected in the Sault Ste. Marie Area. These samples appear to have no influence from the Xstrata smelter as they lie along a mixing line between the Essar Steel point source and U. S point source with no influence from the Sudbury area. These samples are located the furthest from the Sudbury Area and border the Midwestern states. The samples located in the Sudbury area (green and red) are not influenced by any mixing with the Essar Steel point source. These samples are located on a mixing line between the Xstrata Point source and the U. S point source. As samples were collected during the Vale Inco Shutdown, samples located in the area are only influenced by Xstrata and the U.S. aerosolic emissions. Samples collected between Sudbury and Sault Ste. Marie that are located closer to the Sudbury area have lead isotopic signatures that are more similar to the U.S with distance from the Xstrata point source. Samples located between the two northern point sources are influenced by the U. S point sources, with only a minor influence from the northern point sources. Samples located between Sault Ste. Marie and Sudbury and closer to Sault Ste. Marie are slightly influenced by Essar Steel and Sudbury emissions, with the major influenced from the U.S. coal-fired station emissions.

Figure 3 represents those samples collected around the Vale and Falconbridge smelter during the Vale operational period. The data illustrated indicates the small differences in sample

isotopic signatures collected around each point source. The Copper cliff signature is more similar to the U. S signature.

Snow samples were collected around Vale Inco and Falconbridge smelter in the same locations both during the Vale Inco smelter shutdown and after the smelter started back up. Table 7 shows wind gust direction and snow accumulation during the sampling period. Samples in the Sudbury area were collected between Jan 15th and 20th. Despite prevailing winds from the SW, The seasonal winter Northern winter winds are shown as gusts during most days that accumulated snow deposition.

Table 12. Sudbury Area Record of Average Snow Fall and Directional Wind Gust during the Sampling Period

Date	Total Snow (cm)	Dir of Max Gust (deg)
03-12-2009	14.4	360
04-12-2009	2.4	
05-12-2009	2.6	
09-12-2009	14.2	70
13-12-2009	1.8	170
14-12-2009	3.2	
15-12-2009	1.2	
20-12-2009	4.2	
21-12-2009	1.1	
26-12-2009	3	
27-12-2009	3	
28-12-2009	4.8	350
31-12-2009	12.2	
01-01-2010	6.6	330
02-01-2010	0.8	340
03-01-2010	0.8	340
04-01-2010	0.4	350
05-01-2010	2.4	350
06-01-2010	0.2	
11-01-2010	2.4	30
19/01/2010	1.4	

All sample sites were identified by GPS coordinates. Theoretically, during the shutdown, the Vale Inco Smelter aerosols would have been dispersed from the local atmosphere and the signature would have reflected the influence of the Xstrata Falconbridge site smelter operations. During the Vale shutdown one would also assume that as the Vale Inco signature is diluted from the atmosphere that the U. S fingerprint would be more prevalent.

Figures 4 and 5 illustrate that there is no visible difference between the samples taken before the shutdown and after the shutdown. As seen in figure 3, there are differences between the isotope ratios of the two point sources although similar feedstock. The U. S signature may be mixing with the samples collected during the shutdown not allowing for a separation in ratios to be illustrated. Falconbridge is located closer to the top left of the figure while Copper Cliff is located at the bottom right, in line with the U. S point source. During the shutdown the sample signature should locate themselves closer to the Falconbridge point source (top left) and during the operational period the samples have signature that include the Vale Inco point source (bottom right). Instead of the signatures separating during an operational and non-operational period they mix. This is because during the non-operational period when the samples should move to the top right of the graph towards he Falconbridge signature, the samples are pulled lower to the U. S signature thus creating a blend that cannot be differentiated.

4.4.2 S-N Transect Discussion

The major point source emitters along this transect are the Vale Inco Smelter Complex and the Xstrata Falconbridge Smelter Complex. Some of the minor contributors to lead along this transect are:

Lake Shore Gold Corp Bell Creek Complex (13 kg/yr)

Goldcorp Canada Dome Mine (4.9kg/yr)

Xstrata Nickel Montcalm Mine (0.033kg/yr)

Figure 6, under section 4.3.2 S-N Transect results, shows a three way mixing model of the two major point sources, as well as the average U.S point source. Snowpack samples collected in proximity to the minor point sources listed above have no noticeable local fingerprint, but rather display the signatures from mixing with other major point sources. As shown in figure 6, each major point source is distinct from each other. The Xstrata Timmins Metallurgical site (blue dot), has a signature that is distinct from all other sample signatures located along this transect. The Timmins Metallurgical site is the largest Pb emission point source in northern Ontario. Samples collected along this transect should have an isotope signature that involves mixing with this signature. This would be expected because primary wind direction that brought snow deposition was mainly from the north. What is observed in figure 6 may be explained by prevailing winds from the south west that are still effective. The Xstrata Timmins smelter operations has a high annual emission of lead and therefore maintains its own distinct signature. Sudbury operations (red dot) also has a distinct fingerprint that is dissimilar from the USA average. The samples labelled with triangles in red and green are samples not in direct proximity to a point source but collected between the two major point sources. Graph 6 displays that snowpack samples not in close proximity to a major point source are impacted by the U.S sources as distance from other northern point sources increases. The snowpack from sites that are the furthest from the US border still take on a signature more representative of the US than either Timmins or Sudbury smelting Operations, an observation especially evident when looking at the samples collected in Kapuskasing, located approximately 150km north of Timmins.

The data points in figure7 show the annual precipitation isotopic values representing the average for the U.S, Canada, Northern Ontario and Northern Ontario point sources. The average Pb isotopic ratios for samples collected in northern Ontario is expected to be located between the US and Canadian end-member compositions, indicating binary mixing between Pb emissions from the two sources. The field representing average Canadian anthropogenic emissions (shaded red) is taken from (Sturges & Barrie, 1987) and (Carignan j, 1995) and the field representing average US anthropogenic emissions (shaded dark blue) is taken from (Veron, Church, Patterson, Rel, & Merril, 1992) and (K.J.R, Chisholm, Boutron, Candelone, & Patterson, 1994). The northern Ontario average is taken from data collected from snowpack and is shaded in green. The data for samples in this study does not represent a weighted average between the U.S and Canada. This is because the air masses contributing to northern Ontario snowpack reflect the major contribution of Pb releases from minerals smelting and refining processes. Northern Ontario point sources were also plotted illustrating why these samples do not represent a weighted average between Canada and the U. S. The major point sources in northern Ontario are the Xstrata Kidd Met Site and the Sudbury Xstrata Smelter. The northern Ontario average thus lies closer to these point sources. Essar Steel is a minor but still significant contributor. Located in Sault Ste. Marie this company borders the Midwestern states giving rise to a signature more influenced by the coal fire power plants.

Figure 7. $^{208}Pb/^{206}Pb$ versus $^{206}Pb/^{207}Pb$ mean monthly data for precipitation samples

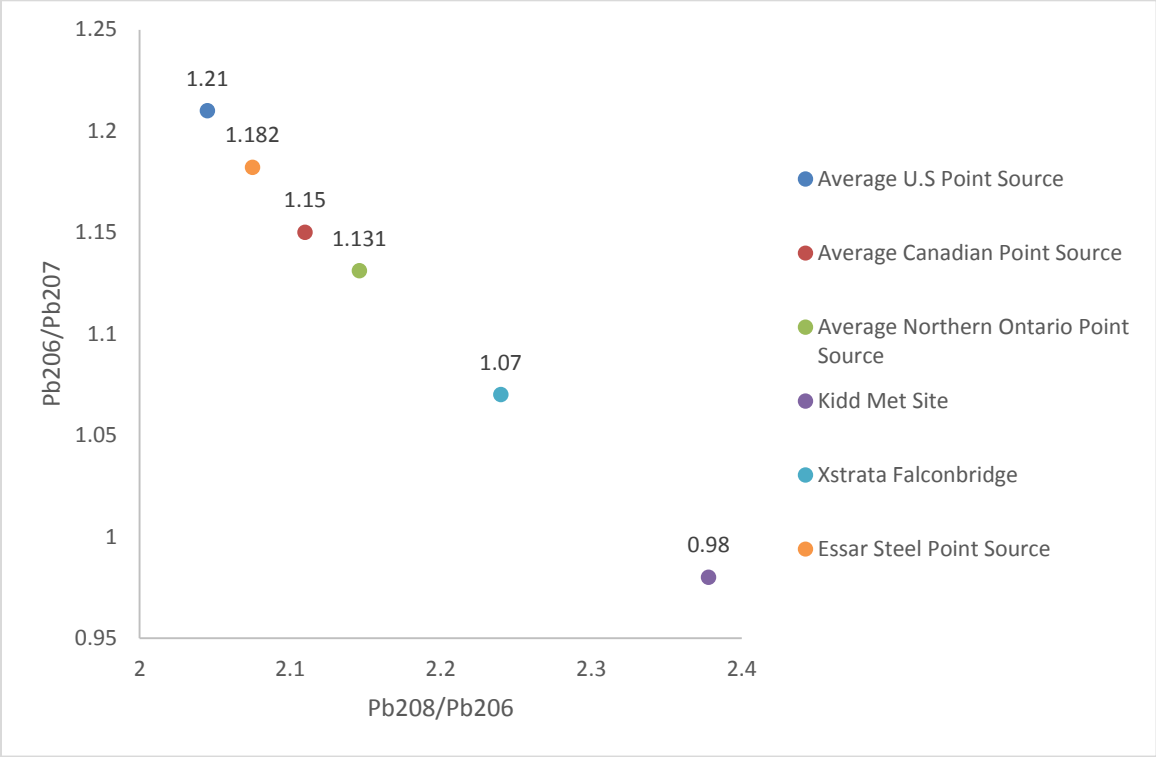
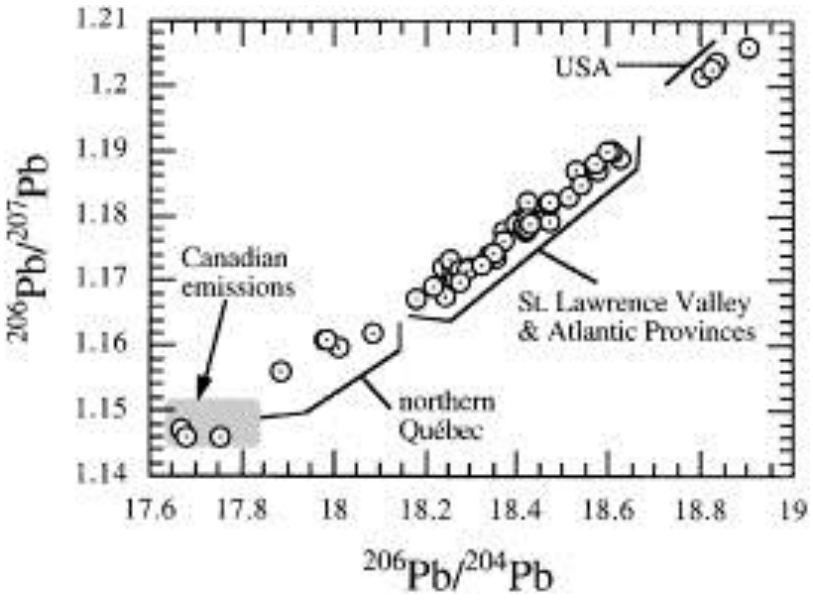


Figure 8 shows data points from different studies throughout Canada. All the data in this Pb isotope diagram define a linear array suggesting mixing between Canadian and USA Pb emissions. The Canadian emission field include data from (Carignan j, 1995) (J. Carignan, 2002)

Figure 8. Binary Mixing between the U.S and Canada showing a linear array (Carignan j, 1995)



The data illustrated in figure 8 from two external studies also indicate that the isotopic signature difference between the US and Canada are both very distinct, as is the signature from northern Ontario.

4.5 Conclusion

Snowpack samples located along the W-E transect from Sault Ste. Marie to the Sudbury regions of Northern Ontario tend to reflect an isotope signature of the coal fired power stations from the neighboring Midwestern states. One would expect the isotope signatures of Xstrata Falconbridge which emitted 5074 kg of Pb in 2010 to have a major influence on the signature from neighboring communities along the W-E transect. The S-N transect illustrates similar trends to that of the W-E transect. Samples not in close proximity to major point source have a signature mostly influenced by the diffuse US power generation sources. Snowpack samples collected at greater distances from the US border indicate that the ratios show no trends of decreasing US signature with distance, an observation confirmed with samples collected from as the Kapuskasing region approximately 400km from the US border. Although the dominant surface wind gust direction is from the north, the prevailing southwestern winds transporting the snow bring an overwhelming amount of transboundary Pb pollution to Northern Canada. This dominant US contaminant load means that it is very difficult to determine the mixing patterns between northern Ontario point sources.

5.0 Tracing Lead in Rainwater

5.1 Introduction

Pollution from long-range transport and local emission has major impacts on the composition of Pb isotopes in both rainwater and aerosols. Anthropogenic sources of metals

such as industrial activity, coal combustion and automobile exhaust have become dominant sources affecting the chemical composition of aerosols and rainwater (Negrel, 1998). An advantage of monitoring rainwater is the ability to estimate atmospheric depositional fluxes that can originate from inputs from pollution sites, air mass origin and transport pathway and transport time (Hoffman, 1977). The Pb isotopic composition in rainwater depends heavily on several factors, including source inputs, distances from industrial areas, traffic density, prevailing wind direction and rainfall intensity (Halstead, Cunninghame, & Hunter, 2000). As the rainwater examined in this study was collected during the summer of the shut-down of the Vale Inco smelter operations in Copper Cliff, Ontario, it provides an advantage to be able to monitor the atmospheric washout of lead from that particular point source. The isotopic composition should change over time as the amount of lead from that particular point source gets atmospherically diluted.

Plate 11. Weather Station to monitor seasonal wind patterns and rainfall

5.2 Methodology

In the summer of 2009 rainwater samples were collected at two different sites in northern Ontario; Falconbridge and Lively. The rainwater samplers were continuous open collectors located 1.5m above the ground to collect bulk deposition and limit debris from the ground (Figure 12). The samplers consisted of a 19cm diameter polyethylene funnel connected through a polyvinylchloride pipe 1.5 m long to a 2L collection bottle. The funnel components were all soaked in a 10% nitric acid bath overnight, then washed three times with deionised water. The bottles were buried beneath the ground at each collection site to minimize light induced alteration of the collected water, and also to keep the sample cool to prevent evaporation. A styrofoam ball was placed on top of the opening of the 2L collection bottle so that the collected sample was only exposed to the atmosphere in the event of a rainfall. During a rainfall the water would be collected in the funnel, run down the 1.5m PVC pipe to be stored in the collection bottle. The water would then float the Styrofoam fall upward, thus opening the bottle to allow water entry. A polyethylene screen was placed over the funnel to exclude insects and large debris. The collection system was supported from disturbance in windy conditions with a steel rod. The following plate is a schematic of the rainwater collection system.

Plate 12 Schematic of Rainwater Collection System

After each significant rainfall the bottle was collected and replaced by a clean one. The samples were filtered, acidified and analyzed by ICP-MS using the same procedure as the snowpack samples (see section 4.2, snowpack methodology). Rainwater samples were ran with snowpack samples and QA/QC data can be seen in Appendix B. Table 12 shows the standard deviation and percent relative standard deviation of the average rainwater samples that were ran with the snowpack samples. Table 14 shows the standard deviation and relative standard deviation NBS982, that was ran as an external monitor along with the snowpack samples.

Table 13: Average Standard Deviation and Relative Standard Deviation of Rainwater Samples That Were Run with Snowpack Samples

Isotope Ratio	^{207}Pb / ^{206}Pb	^{208}Pb / ^{206}Pb	^{206}Pb / ^{204}Pb	^{207}Pb / ^{204}Pb	^{208}Pb / ^{204}Pb
Standard Deviation	0.0049	0.0113	0.2069	0.1825	0.4323
Std Dev Range	0.0013-0.014	0.0038-0.0290	0.0469-0.5550	0.0529-0.4738	0.1058-0.9907
%RSD	0.5617	0.5337	1.1401	1.1596	1.1303
%RSD Range	0.1505-1.679	0.1658-0.86758	0.2920-2.989	0.3440-3.024	0.2780-2.582

Table 14 : Standard Deviation and Relative Standard Deviation of External Rainwater Reference Material NBS 982

NBS 982	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$
average	0.46695	1.00005	36.727
stdev	0.00025	0.00081	0.057
rsd	0.054	0.081	0.155

5.3 Results

The following table displays the surface atmospheric information collected by the weather station during each rainfall event at each sampling location. A value of O indicates that the wind speed was minimal for that sampling day. Sample collected in bulk represent a series of rainfall events between a particular sampling period.

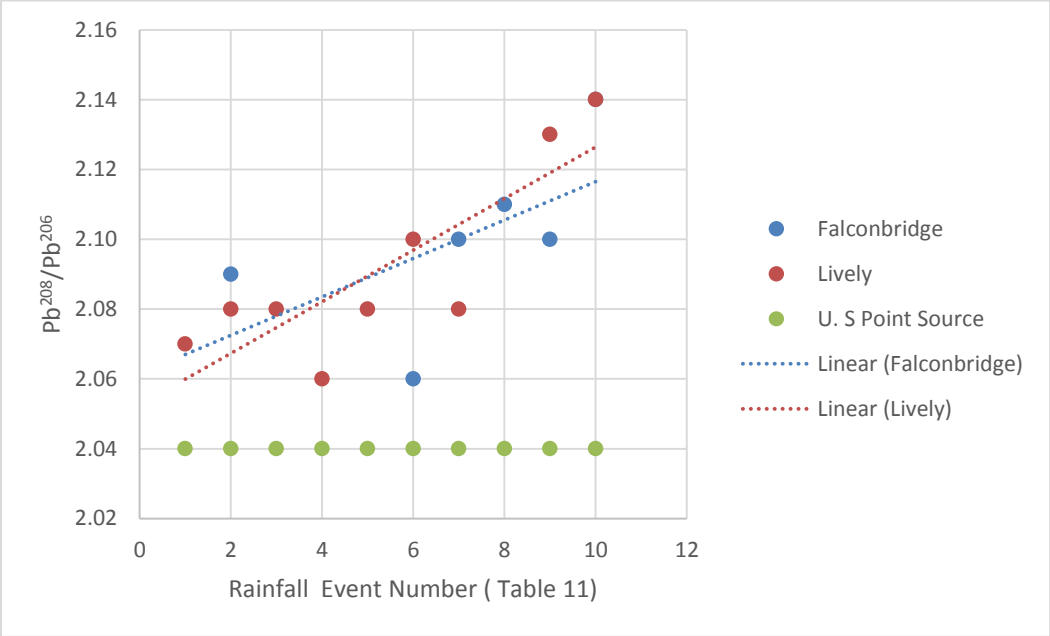
Table 15. Rainwater sampling event data and location

Rainfall Event Number	Sampling Period (D/M/Y)	Wind Direction	Pb^{208}/Pb^{206} Falconbridge	Pb^{208}/Pb^{206} Lively
1	28/06/2009	SW-S		2.07
2	11/07/2009		2.09	2.08
3	17/07/2009-18/07/2009	0		2.08
4	23/07/2009-24/07/2009	NE		2.06
5	25/07/2009-	SE		2.08

	26/07/2009			
6	09/09/2009 (bulk)	SE	2.06	2.10
7	27/09/2009- 28/09/2009	SE	2.10	2.08
8	03/10/2009	SE	2.11	
9	22/10/2009- 19/11/2009	NE	2.10	2.13
10	26/11/2009- 29/11/2012	NE	2.14	2.14

The Graph 9 displays the Pb^{208}/Pb^{206} ratio for atmospheric washout of Pb over a series of rainfall events, with the data increasing over time. The U.S fingerprint is continuous over time in this case. Rainfall event numbers correspond to those listed in Table 11.

Figure 9. Atmospheric washout of Pb^{208}/Pb^{206} in Falconbridge and Lively, Ont



The prevailing wind direction within the Sudbury area normally follows a south-west to north-east transect, however, seasonal patterns can be observed, with winds usually blowing from the northwest to north during the colder winter season (Potvin, 1976).

5.4 Discussion

Rainfall was collected after a series of precipitation events between July 7th 2009 and November 30th 2009 (see Table 11). Sampling was conducted during the shutdown of the Vale Inco Copper Cliff Smelter. As the rain water event number increased one would expect the isotopic signature to represent the isotopic fingerprint of other sources more and more as the relict signature of Vale Inco in the local environment was continuously washed out. This graph depicts a washout and a change in $Pb^{208}/^{206}$ over time, with an increase from 2.06 to 2.14 over the collection period. In Figure 9 is can be seen that Pb is getting washed from the local atmosphere by precipitation there is a decreasing influence from the closed Vale Inco operations signature. As the Vale Inco signature gets diluted, the impact of the US Signature should have more of an impact. The US signature is illustrated by the trend line in green. The trendlines in Figure 9 indicate that there is, however, a deviation in the regional trend line at the sample sites away from the US trend line with increasing precipitation washout over time.

The isotopic ratios for $Pb^{208/206}$ are higher in the winter months than the summer months. In the winter months (rainfall event number 8, 9, 10) the ratios are in the range 2.11-2.14 from table 11 and in the summer months (rainfall event number 1-7) the ratios are in the range 2.06-2.10. This Pb isotopic signature difference is explained by differences in prevailing wind directions and seasonal wind patterns. The prevailing wind direction within the Sudbury area normally follows a south-west to north-east transect, however, seasonal patterns can be observed (Potvin, 1976). For example, during the summer months the winds are typically from the southwest, south and west (Potvin, 1976). During the colder winter seasons, the winds are usually blowing from the northwest to north (Potvin R, 1976). Wind direction is shown in Table 11 during each sampling event number. The observations of Potvin (1976) are evident in the data collected

during the seasons of each rainfall sampling event. During the summer months the isotopic signature is very similar to the signature from the US. Since the prevailing winds in the summer come from the southwest, south, and west, the weather systems bring Pb aerosolic transboundary pollution from the coal fired power plants in States that border with Canada. In the winter months the prevailing winds are from the northwest to north. As there is not a dominant regional point source for Pb aerosolic emissions upward, the isotopic signature is not influenced as much from transboundary pollution sources carried from the U.S. In figure 9 the samples have a signature that increasingly becomes more distinct from the U. S signature as more of the Vale signature is washed from the atmosphere. The data in Figure 3 indicate that the emissions from the Vale and Falconbridge smelting operations have dissimilar Pb^{208}/Pb^{206} ratios. The Pb^{208}/Pb^{206} ratios for Falconbridge are higher as are the ratios in Figure 9 as Vale is washed from the atmosphere. The average isotope ratio for Falconbridge in the snowpack is 2.21 and the average for Vale is 2.13.

5.5 Conclusion

By monitoring atmospheric fallout using rainwater the data in this study illustrate that as the lengthy shutdown of the Vale Inco Copper Cliff Smelter in 2009 allowed ongoing atmospheric washout of the Pb aerosols from the smelter footprint, allowing the signature to become prevalent. Seasonal patterns were observed with prevailing wind direction and contamination from transboundary pollution during the summer sampling season. It cannot be determined from Figure 9 whether or not the Vale signature is being diluted from the atmosphere and the Falconbridge signature is becoming more prominent, or if the increasing trend in $Pb^{208/}Pb^{206}$ arises from seasonal wind patterns changing the levels of transboundary pollution from the coal fired power plants from the summer to winter months.

6.0 *Tracing Lead in Lichen*

7.1 Introduction

From as far back as 1866 lichens have been used as bio-monitors of pollution (Nylander, 1866). Lichens are used to measure atmospheric deposition because they derive their nutrients, metals and contaminants solely from wet deposition (Geiser, 2009) . Environmental bio-indicators, such as lichens, represent a complementary tool for expensive environmental monitoring systems, and could also overcome some of the shortcomings associated with the direct measurements of pollution.

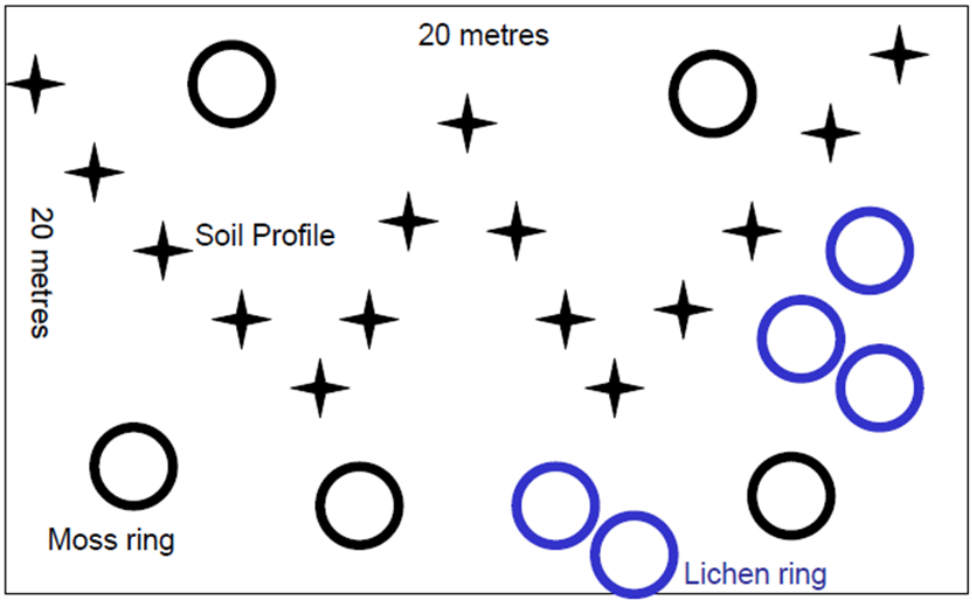
The use of lichens as very sensitive bio-indicators of heavy metal contamination as a technique for surveying atmospheric metal deposition was developed in the late 1960's (Ruhling & G, 1969). The technique is based on the fact that lichens only have a rudimentary root system, so the uptake of elements comes mostly from the atmosphere, with the bulk of the nutrients for metabolism being obtained from rain water deposition containing associated airborne particulate material (Berg & Steinnes, 1997).

Unlike higher plants, lichens lack the waxy cuticle and stomata and readily absorb gases and dissolved substances in the air through their surface (Loppi, Ivanov, & Boccardi, 2002). The tracing of epiphytic lichens and their role as biomonitors of trace element air pollution is now widely acknowledged, however, two shortfalls associated with the use of epiphytic lichens as biomonitors include their slow metabolism rate and unknown age, both which complicate interpretations of signals of atmospheric Pb on short and precise time scales.

6.2 Methodology

The lichen sampled for this research project was a fruticose species (*Cladonia Rangiferina),* most commonly known as reindeer moss. This lichen waschosen because they are sufficiently abundant in northern Ontario. Samples were collected during August to September of 2009, the end of the vascular plant growing season. For this study, 28 sites were sampled along two main transects, an West- East transect between Sault Ste. Marie and Sudbury, Ontario, and at South-North transect that extended from Sudbury through Timmins to Kapuskasing, Ontario. Five samples were collected at each geo referenced site which was accessed off primary and secondary highways or forestry and mining roads that allowed reasonable and safe access to woodlands. All sample sites were located at least 250m from the road allowance and collected in open areas, devoid of large trees, to optimize input from aeolian sources. The sampling plan allowed for a collection up of to five representative samples of the dominant lichen species at each sample site (see plate 14). Plate 14 shows the sampling technique of lichen that was used to prevent sampling bias and to obtain a representative sample.

Plate 13. Lichen collection sampling pattern



All sites were geo-referenced using a Garmin GPS and location plotted on standardized maps. A series of site and sample digital photographs were collected at each sample site and a brief site herb, shrub and canopy layer species list was also recorded.

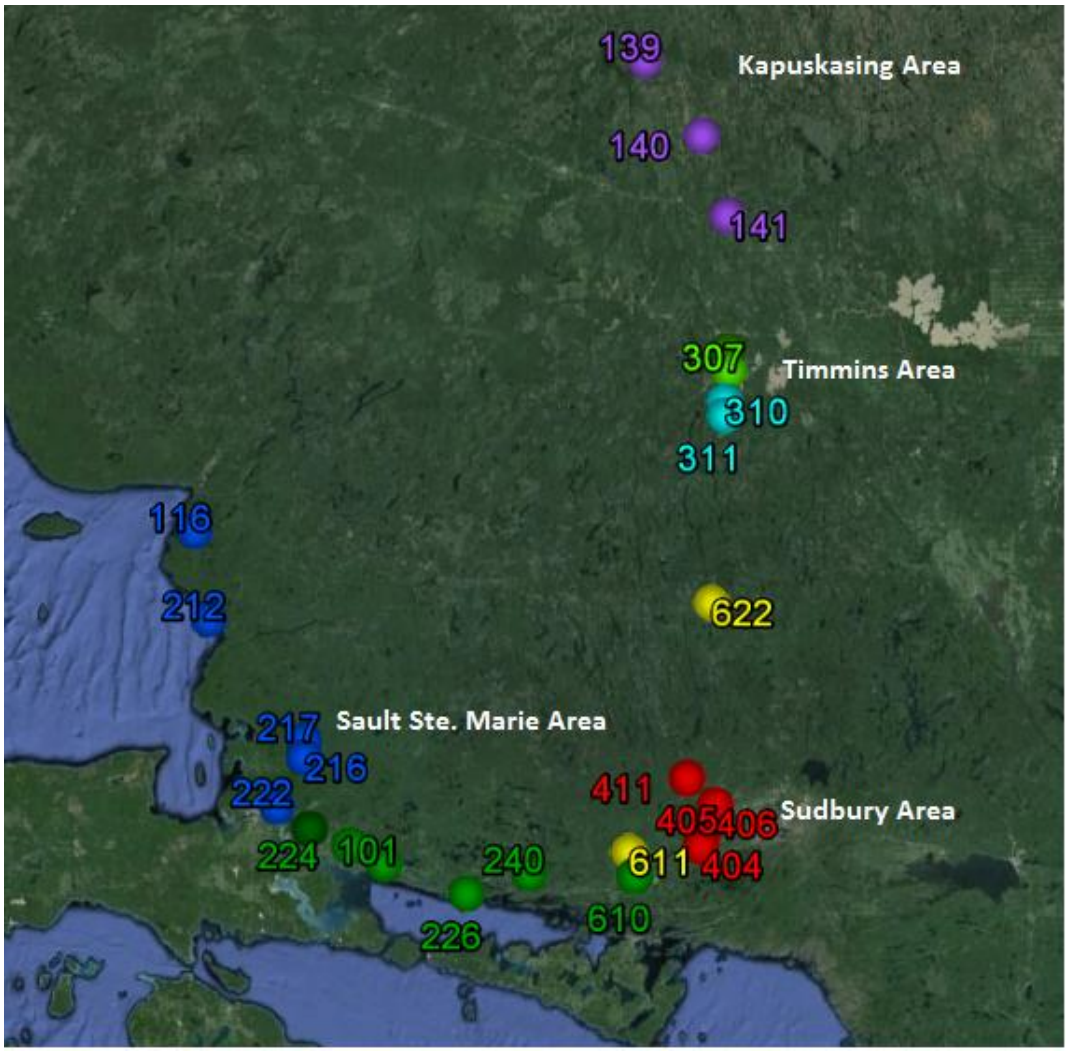
The lichen tissue was always handled with clean latex gloves, and each set of gloves discarded after the handling of each sample to avoid cross contamination. The sample was collected from the inside of a 15cm diameter stainless steel ring, and placed into a paper bag to facilitate transport and drying (Plate 15).

Plate 14. Sampling tools for lichen collection

On return from the field, the paper bags containing the moist samples were opened in a clean room at Penguin Research Centre in Naughton, Ontario, and air dried at room temperature (25 C) for several days. The air dried samples and paper bag were stored for subsequent analysis at the Elliot Lake Field Research Station ISO 17025 analytical facility in the Willet Green Miller Center (WGMC

Plate 16 shows the two main sample transects with the sampling sites plotted from their respective GPS coordinates.

Plate 15. Subsample of Lichens taken from the MOSS Project



The dried samples were cleaned and debris was carefully removed from their substratum using nylon tweezers. Cladina lichen has a growth pattern that makes it easy to distinguish the annual incremental growth. The Cladonia lichens generally produce a new branch each year, so that age of a clump can be estimated by counting back through the major branching along a stem (Andreev, 1954). Only in the fructose Cladonia and Cladina lichens which branch once each year can age be readily determined (Andreev, 1954). The current year's growth, namely the uppermost whorl of branches was cut off and separated from the rest of the cladina, for analysis separate from the bulk plant (see figure 16).

Plate 16. The uppermost whorl of branches which was separated from the rest of the cladina.

Only the living actively growing tissues from the upper part of the podetium were used for digestion and analysis. Senescent tissues, recognized by their duller, greyer color, were carefully

removed. A single podetium which represents a natural individual unit in the interwoven mat of cladina was used in each experiment. .

The annual upper whorl of growth was dissected from the rest of the podetium again using nylon tweezers. The stem and the whorl were individually stored in polyethylene bags. Both the stem and whorl were ground separately using a ceramic pestle and mortar into a fine powder. To avoid contamination between grinding the pestle was covered with a polyethylene bag and the sample was left in the polyethylene bag during grinding in the mortar. After each sample the pestle was covered with a new bag. Three replicates of both the stem and whorl were taken from three individual lichens. After the samples were ground 0.5 ± 0.02g of the sample was weighed out on a calibrated balance into clean 50ml Teflon™ digestion tubes, and digested with 6 ml HNO_3(c), 2 ml HCl (c) and 1 ml HF. The HF was used in the digestion to digest silicates that are present in the stomata of the plant. The samples were predigested in a fume hood for 24 hours at room temperature to digest organic matter prior to heating, and then digested in a programmable digestion block (HotBlock pro). The block was ramped slowly to 105°C and held there for 2.5 hours, and cooled to room temperature prior to dilution to 50ml with ultrapure water from a Milli-Q water system. The tubes were capped, shaken to mix the contents, and allowed to settle overnight prior to decantation of the supernatant solution. The samples were diluted 10 fold again with ultrapure water prior to analysis by ICP-MS. A 2% HNO_3 digestion blank, together with a standard reference material (NIST SRM 982) was analyzed with every four samples. The SRM was an equal atom lead isotopic standard wire (SRM 982) was purchased from NIST (National Institute of Standards and Technology), digested with ultrapure HNO_3 and diluted to 10ppb.

6.2.1 Instrumentation and Quality Control

The determination of isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb completed using a Varian quadrupole ICP MS instrument equipped with a peristaltic sample delivery pump, with A new glass concentric spray chamber, sample cones, glass nebulizer, and new pump tubing were installed for this research project to minimize carry over from previous sample analysis. The spray chamber and interface were cooled at 10°C with manual sample introduction to the uptake tubing. All samples were transferred into pre-cleaned Nalgene ™ Falcon tubes. The tubes were washed three times with 2% optima grade ultra-pure nitric acid and rinsed three times with ultra pure water. The instrument was rinsed with a 2% nitric acid solution until Pb counts on the blank were lower than 500 counts per second. The ICP MS was optimized for maximum sensitivity with ^{209}Bi, a mono-isotopic element with a mass close the Pb isotopes being analyzed. The counts on a 2% acid blank, a 1ppb and a 10ppb ^{209}Bi solution were 500 cps, 110,100 cps, and 2,110,212 cps respectively. These sample counts indicated that the instrument was performing at a sensitivity level well suited for Pb analysis (1.5 million counts per ppb). To determine the washout time needed between samples, the isotope ratio $^{208}Pb/^{206}Pb$ was monitored on SRM 982. The atomic abundance ratio of $^{208}Pb/^{206}Pb$ on NIST 982 is 1.00016 ± 0.00036. The natural atomic abundance of $^{208}Pb/^{206}Pb$ in NIST 981 is 2.1681 ± 0.0008. The differences in these abundances enabled the monitoring of the wash time would be monitored by looking at the changes of the ratios over time from the NIST 982 standard value (1.00016) to the background natural ratio value for NIST 981 (2.1681). This experiment demonstrated that any memory affect was avoided with a wash time of 1 min between samples to eliminate any residual Pb contamination from the previous sample. Repeated measurements of a 10ppb solution of NIST 982 Pb standard yielded an external reproducibility of ±0.01 σ. Accuracy of the Pb-isotope ratios were <0.16 for $^{207}Pb/^{206}Pb$ RSD, <0.29 for $^{208}Pb/^{206}Pb$ RSD and <0.17% for $^{206}Pb/^{204}Pb$. This

measure of accuracy was determined using the RSD determined from multiple analysis of NBS-982. NBS 981 lead wire standard was weighed (1.000g), dissolved in 199ml of 5% HNO_3 in a thoroughly pre-cleaned 200ml polypropylene bottle. Both the NBS 981 and 982 solutions were diluted to yield 1.5 million counts on the 208Pb channel. A 5.25ppb solution of NIST 982 yielded approximately 1,420,000 counts and 2.5ppb of NIST 981 yielded approximately the same. The NBS 981 was used to correct for mass bias and NBS 982 was used to check for accuracy. During the sample analysis a 2% nitric acid blank was ran every five samples, before and after each NBS 981 analysis. The NIST 982 was analyzed following every 15 samples along with the digestion blank. The digestion NBS 981 solution was ran every 25 samples. The repeat analysis of a reference solution (^{209}Bi) was undertaken as an external drift monitor. Results of this analysis can be seen in Appendix.

6.2.2 Correction Procedure

ICP-MS is a suitable method for determining Pb isotope ratios as long as factors such as mass discrimination and blank correction are measured in order to get reliable data. The mass discrimination technique used was based on the addition of two NIST SRM Pb samples (NIST SRM 981 and 982) that were analyzed after every 4 samples. This method was chosen to minimize bias and drift in the Pb isotope ratios. Appendix F is an example of the equations used for blank correction and mass discrimination.

As it can be seen from these equations the Pb isotope ratios were corrected using the NIST SRM 981. The reference material NIST SRM 982 was then used as an external quality control standard that was ran every four samples. The technique used for analysis was a bracketing technique where a set of standards and blanks were ran after every 3rd replicate of each sample. This allowed instrumental drift to be corrected for over a short time period.

Sample data of blank corrected counts can be seen in Appendix E, mass bias corrected isotope ratios can be seen in Appendix G and SRM 981, 982 and digested SRM 982 results can be seen in Appendix H. The operating conditions of the ICP MS 819 are listed in Appendix I. Table 16 shows the average, standard deviation and relative standard deviation of the average NBS 981 Standard, 982 Standard and Average for all triplicate analysis of lichen samples.

Table 16: Average, standard deviation and relative standard deviation of all NBS 981 and NBS 982 standards as well as an average of the triplicate analysis of each stem and whorl sample of the lichen.

NBS 981	**Pb^{207}/Pb^{206}**	**Pb^{208}/Pb^{206}**	**Pb^{206}/Pb^{204}**
AVERAGE	0.9043	2.1112	16.6525
Std Dev	0.0016	0.0055	0.0441
RSD	0.1762	0.2601	0.2648
NBS 982	Pb^{207}/Pb^{206}	Pb^{208}/Pb^{206}	Pb^{206}/Pb^{204}
AVERAGE	0.4621	0.9755	35.9606
Std Dev	0.0017	0.0042	0.1878
RSD	0.3713	0.4352	0.5223
Samples (triplicate)	Pb^{207}/Pb^{206}	Pb^{208}/Pb^{206}	Pb^{206}/Pb^{204}
AVERAGE	0.8634	2.0677	17.3830
Std Dev	0.0086	0.0300	0.1218
RSD	0.9904	1.4529	0.7004

6.3 Results

Lichen was sampled along the same transects as the snowpack. The W-E transect consisted of sampling from Sault Ste. Marie to Sudbury. The S-N sampling consisted of those samples collected from Sudbury up through Timmins to Kapuskasing.

6.3. S-N Transect Results

The following is a figure of the sample locations along the S-N transect with numbers corresponding to sample location.

Plate 17. Grey Reindeer Lichen Sampled Along the S-N Transect

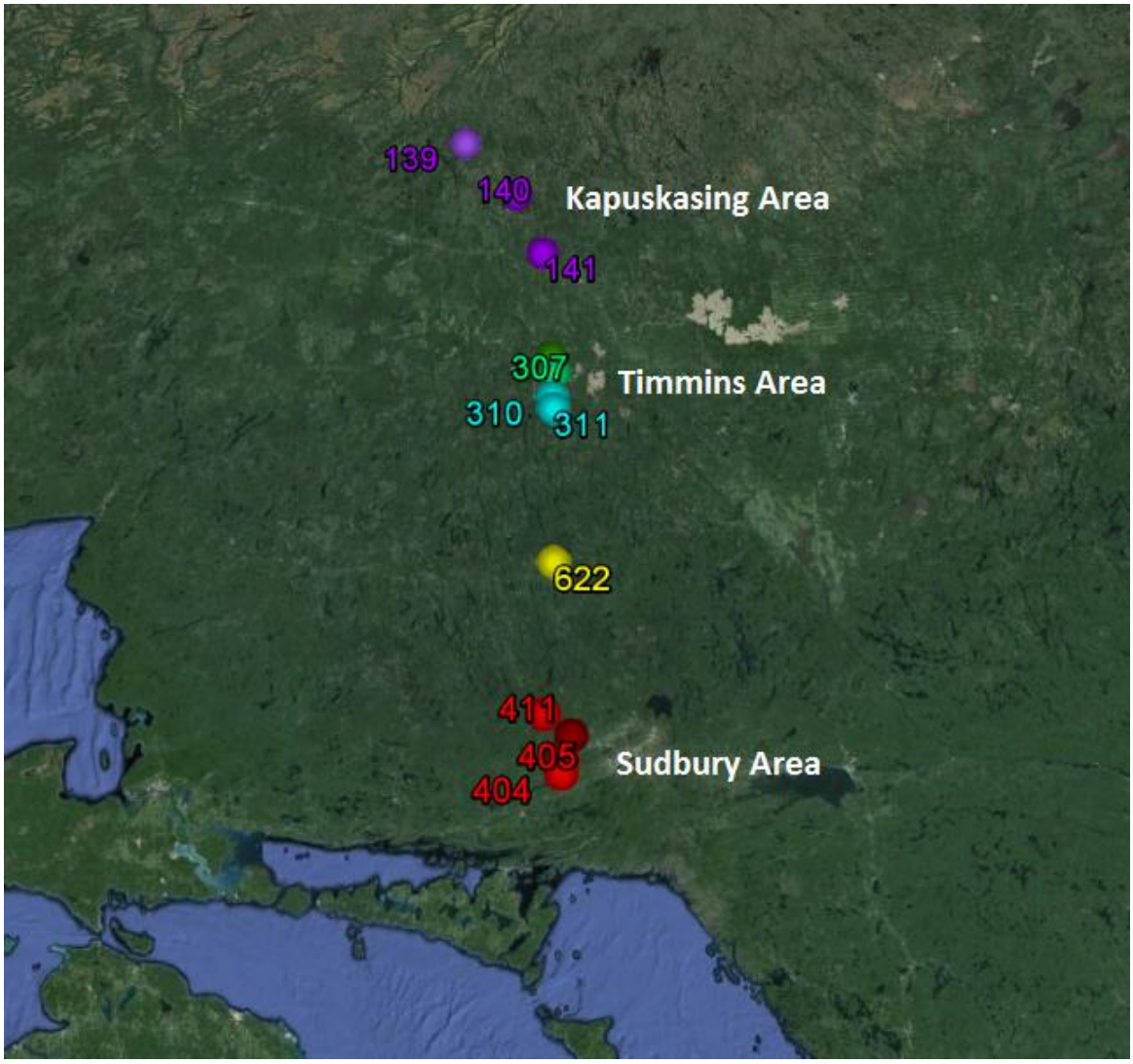


Figure 10 illustrates the isotope ratios of Pb^{206}/Pb^{207} vs. Pb^{208}/Pb^{206} along the North-South transect in the stem of the lichen. The N-S transect includes samples taken from Sudbury up through Timmins to Kapuskasing, Ontario.

The potential major point sources along this transect include: Xtrata Canada Corporation-Xstrata Copper Canada Division, Kidd Metallurgical Site (area in figure 11 circled in brown); Xstrata Nickel-Montcalm Mine; Vale Inco Smelter Complex (area in figure 11 circled in black); Xstrata Falconbridge Smelter Complex (area in figure 11 circled in black)

Figure 10. Grey Reindeer Lichen 3-Way Distribution Graph from Sudbury up through Timmins to Kapuskasing showing groupings of signatures by area

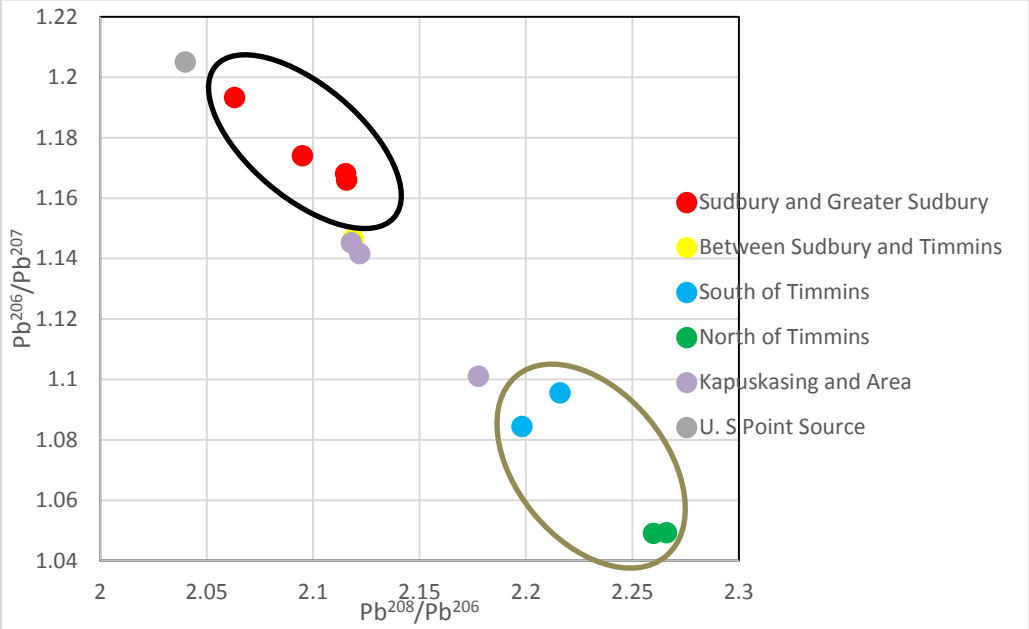


Table 17. Grey Reindeer Lichen Pb $^{208}/^{206}$ and Pb $^{206}/^{207}$ data from Sudbury up through Timmins to Kapuskasing

Sample ID	Location	GPS Coordinates Latitude	GPS Coordinates Longitude	*Corrected Pb206/Pb207	* Corrected Pb208/Pb206
404 stem AVG	West of Whitefish north of Hwy 17	46° 24' 27.55"	81° 28' 23.24"	1.166	2.116
405 stem AVG	North-west of Whitefish	46° 27' 54.2"	81° 27' 34.91"	1.174	2.095
406 stem AVG	North-west of Azilda	46° 35' 29.32"	81° 22' 46.72"	1.168	2.115
411 stem AVG	North of Cartier, Division Lake	46° 42' 38.22"	81° 33' 42.19"	1.193	2.063
622 stem AVG	North-east of Westree	47° 29' 13.75"	81° 24' 14.88"	1.147	2.119
311 stem AVG	Coming into Timmins	48° 19' 2.38"	81° 18' 43.85"	1.095	2.216
310 stem AVG	South of Timmins	48° 22' 51.17"	81° 18' 55.5"	1.084	2.198
307 stem AVG	North of Timmins	48° 31' 1.18"	81° 17' 6.71"	1.049	2.266
306 stem AVG	North of Timmins, off of Big Water	48° 36' 12.27"	81° 17' 27.9"	1.049	2.260
141 stem AVG	Greenwater Provincial Park	49° 12' 38.62"	81° 17' 32.81"	1.101	2.178
140 stem AVG	North-west Cochrane	49° 34' 16.16"	81° 27' 58.85"	1.145	2.118
139 stem AVG	North-east of Kapuskasing	49° 54' 43.31"	81° 51' 30"	1.142	2.122
U. S Point Source				1.205	2.040

***Corrected = Blank Subtracted and Mass Bias Corrected**

The data in Figure 11 describe the difference in the Pb^{207}/Pb^{206} isotope ratios between the stem and whorl of the lichen that was sampled during the summer of 2009. Pb^{207}/Pb^{206} was used in this case because the difference between the signatures of the stem and whorl are more apparent.

Figure 11. Difference in Stem and Whorl of Cladina Lichen in Samples Collected Along the S-N Transect

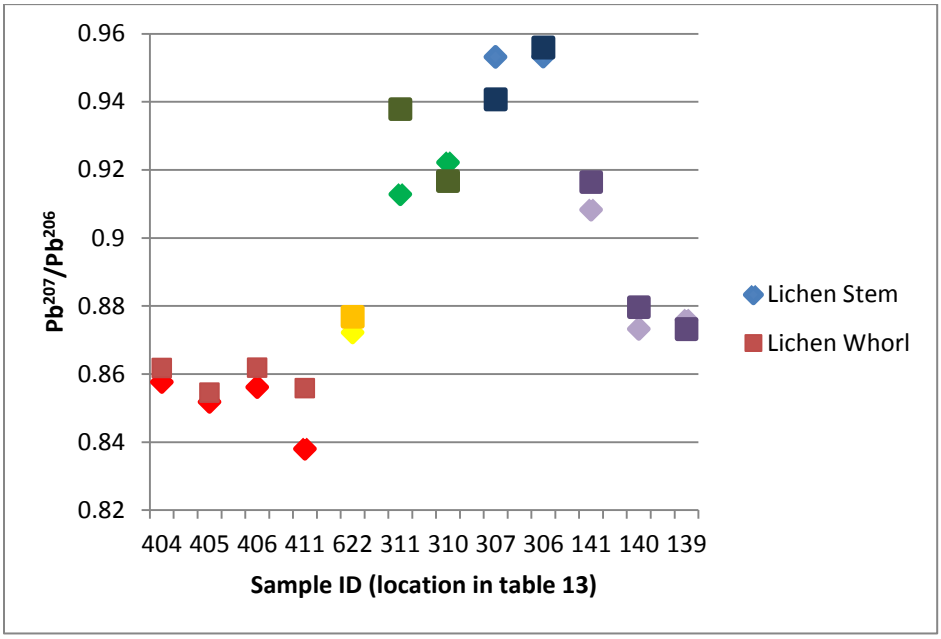


Table 18. Sample data for stem and whorl Pb ratios along the S-N transect. Sample Locators are color matched with figure 11.

Location	Sample ID	Pb207/Pb206 Stem	Pb207/Pb206 Whorl
West of Whitefish north of Hwy 17	404	0.858	0.862
North-west of Whitefish	405	0.852	0.854
North-west of Azilda	406	0.856	0.862
North of Cartier, Division Lake	411	0.838	0.856
North-east of Westree	622	0.872	0.877
Coming into Timmins	311	0.913	0.938
South of Timmins	310	0.922	0.917
North of Timmins	307	0.953	0.941
North of Timmins, off of Big Water	306	0.953	0.956
Greenwater Provincial Park	141	0.908	0.916
North-west Cochrane	140	0.873	0.880
North-east of Kapuskasing	139	0.876	0.873

6.3.2 W-E Transect Results

The following is a plate of the sample locations along the W-E transect with numbers corresponding to sample locations.

Major point sources along this transect include:

Vale Inco Smelter Complex

Xstrata Falconbridge Smelter Complex

Essar Steel Algoma

Plate 18. Grey Lichen sample collection along the west-east transect between Sault Ste. Marie and Sudbury

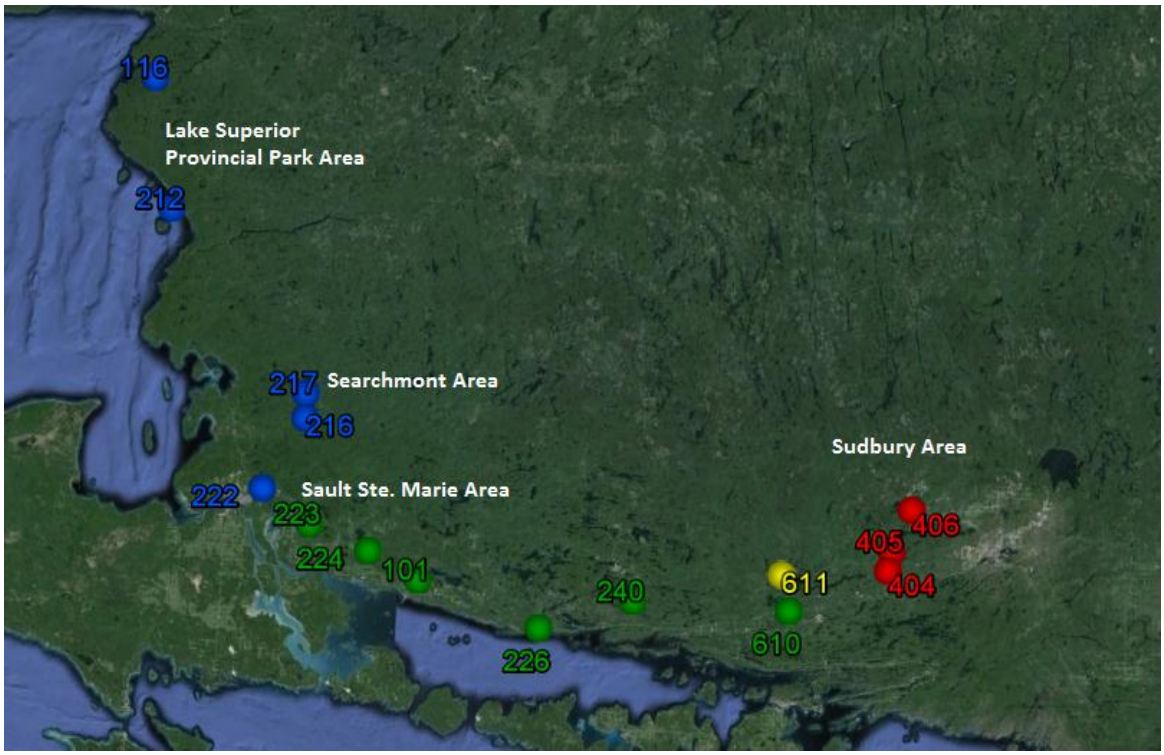


Figure 13 shows a 3-way graph plotting the isotope ratios of Pb^{206}/Pb^{207} vs. Pb^{208}/Pb^{206} along the west-east transect in the stem of the lichen. In this particular graph each sample is effected by

three different variables (point sources). This is notes because all samples do not lay in a linear array. The red data points circled in red represent those samples collected around the Vale Inco Smelter Complex and the Falconbridge Xstrata Smelter Complex. The blue data points circles in grey represent those samples collected around the Essat Steel Plant.

Figure 12. 3-Way distribution of Pb^{206}/Pb^{207} vs. Pb^{208}/Pb^{206} along the west-east transect in the stem of the lichen.

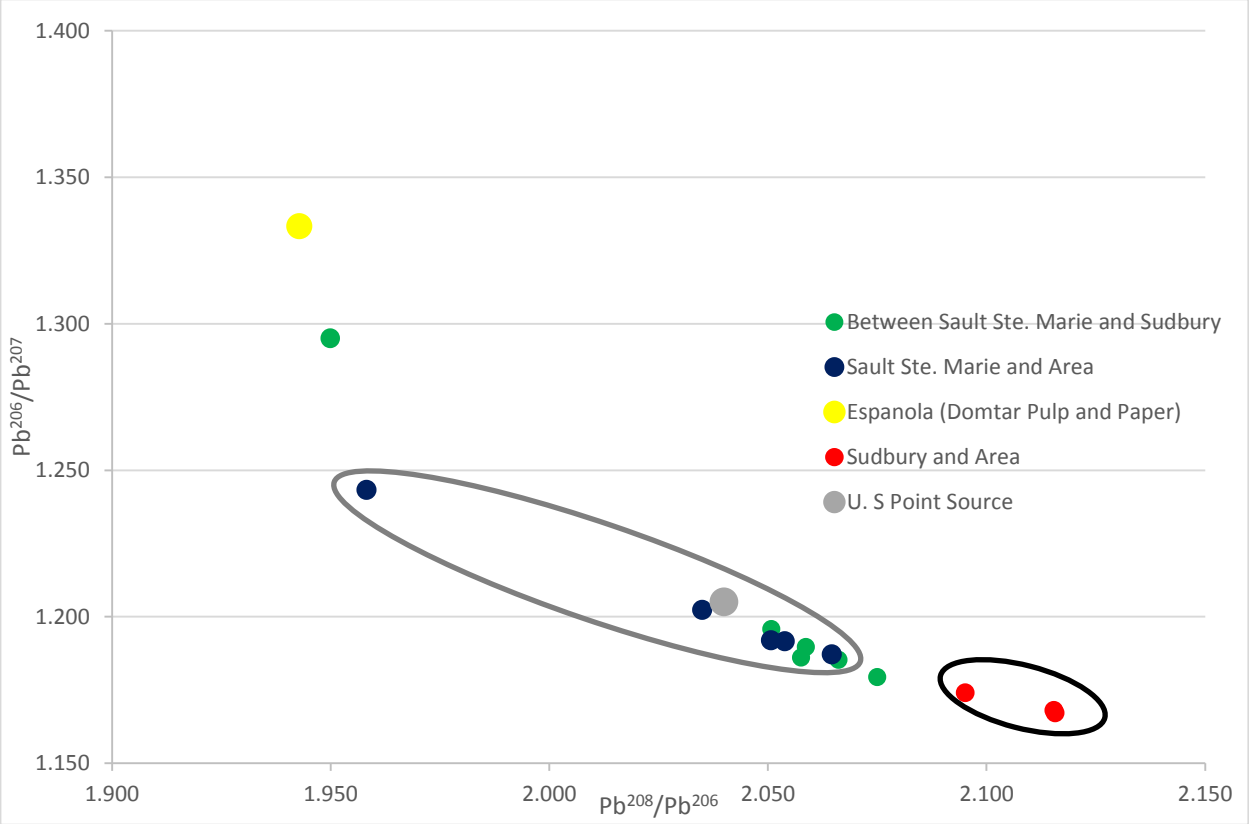


Figure 14 represents a difference in the Pb^{207}/Pb^{206} isotope ratios between the stem and whorl of the grey reindeer lichen that was sampling during the summer of 2009.

Figure 13. Difference in Stem and Whorl of Cladina Lichen in Samples Collected Along the W-E Transect

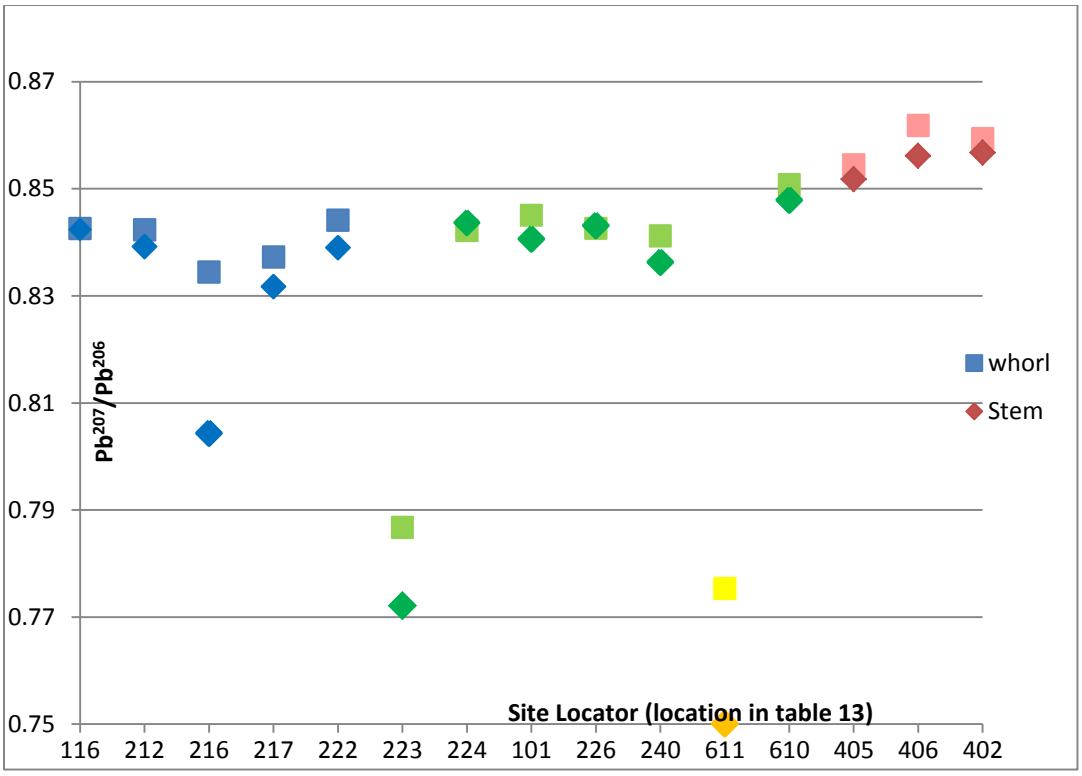


Table 19. Sample data for stem and whorl Pb ratios along the W-E transect. Sample Locators are color matched with figure 13.

Location	Site ID	Pb207/Pb206 (stem)	Pb207/Pb206 (whorl)
North end of Lake Superior Provincial Park	116	0.842	0.843
South end of Lake Superior Provincial Park	212	0.839	0.842
North of Sault Ste. Marie region	216	0.804	0.834
North-east of Wabos	217	0.832	0.837
North-east of Sault Ste. Marie	222	0.839	0.844
South-east of Echo Bay	223	0.772	0.787
North east of Bruce Mines	224	0.844	0.842
North of Thessalon off Hwy 129	101	0.841	0.845
North-west of Blind River off Hwy 17	226	0.843	0.843
South of Eliot Lake	240	0.836	0.841
North-west of Espanola	611	0.750	0.775
North of Webbwood	610	0.848	0.851
North-west of Whitefish	405	0.852	0.854
North-west of Azilda	406	0.856	0.862
North-east of Consiton	402	0.857	0.859

6.4 Discussion

6.4.1 S-N Transect Discussion

Figure 10 shows patterns in grey reindeer lichen that were sampled along the transect between Sudbury up through Timmins to Kapuskasing. The sampling of lichens follow a more linear trend along this transect. Timmins is home to Xstrata Copper Canada Division Kidd Metallurgical Site. This is the largest Pb atmospheric contributor in northern Ontario with emissions in 2009 reported at 23058 kg/yr ((Canada, 2009). One would expect the samples located along this transect to have a major influence from this particular point source. As the samples are collected at closer proximities to the US border, the samples represent a signature that is more and more representative of the U.S fingerprint, as displayed in figure 10 as the grey data point. Even though the impact of the US transboundary pollution is significant it can be seen from figure 10 that each sample area still maintains a distinct signature. When comparing figure 10 and 6 from the S-N transect between lichen and snowpack sampling the graphs follow a similar trend. The differences in the graphs coincide with seasonal weather patterns. Figure 6 represents snowpack samples collected during the winter months. The winter months are associated with winds blowing from the north/Northeast as seen in table 11 for sampling dates from late October to late November. The samples are not as greatly influenced from the U. S point source and therefore are located further from the U. S point taking on more distinct signatures. In this particular graph more mixing between the Timmins Met plant and the samples south to this point source is evident (green triangles in figure 6). The moss samples represent an integration of the summer months and partial snowmelt. With the summer months being the major contributor of atmospheric Pb, the prevailing winds from the S-W bring an overwhelming

signature from transboundary pollution. When comparing figure 6 and 10, in figure 10, there is not as much influence from the Timmins Met Plant. The Sudbury signature as well as the samples taken between both point sources are all located in closer proximity to the US point source.

From this graph it is unclear if each sample location takes on its own fingerprint or if the isotope ratios are changing as a function of distance from atmospheric dilution of the U. S point source. Kapuskasing is the furthest sample location from the border so it would be assumed that it would take on a signature the furthest from the US point source. According to figure 10 this is not the case. Because Kapuskasing is not in the immediate vicinity of a point source atmospheric Pb is diluted in its area. Since prevailing winds in the summer come from the Southwest, South and West (table 11 data from June to Sept), much of Timmins atmospheric Pb is getting blown in Kapuskasing's direction as well as the U. S point source. Figure 10 shows Kapuskasing's fingerprint to be centered on a mixing line between the U. S point source and the Timmins Kidd Met Site.

.

6.4.2 W-E Transect Discussion

Lichen was sampled along the W-E transect between Sault Ste. Marie and Sudbury. Figure 12 maps a three way distribution map showing the results of this transect.

The Espanola data point in yellow deviates from the normal trend. Looking at the graph Espanola data set was sampled in the direct vicinity of Domtar pulp and paper Inc. This company released 19 kg/year of Pb in the environment and 65 kg/yr into the water (Canada, 2009). These emissions from Domtar are small but still prove to be a significant contributor of Pb in its direct vicinity. The green data point that deviated from the set is sampled at location 223. Essar Steel

Algoma is located 15km SW of this data point. The winds in the summer months are bowing from the SW, therefore this data point may be directly influence from the pollution released from the steel plant. Essar Steel Algoma released 194kg of Pb into the atmosphere in 2009. The blue data point that deviates from the set in figure 12 is sample 216. This sample was collected at Searchmont Ski Resort, Sault Ste. Marie. According to the NPRI there is no industry that reported pollution in this area. The chair lifts are run off electric power but use gas as a backup when there is a power outage. This data point may be an outlier in the data set or there is a source of pollution in the direct vicinity that is unknown.

The transect between Sudbury and Sault Ste. Marie has two major point sources and a minor point source. The two major point sources are Falconbridge Xstrata Smelter (5074 Kg /yr) and Essar Steel Algoma (194 kg/yr) (Canada, 2009). The red data set in figure 12 represents the Sudbury area. These points have a signature of their own, most likely representing the Falconbridge Xstrata Smelter signature. The data set in blue represents the Sault Ste. Marie area which does not have a definite fingerprint but rather takes on a signature similar to the samples collected between Sudbury and the Sault. With Xstrata Falconbridge being the dominant point source along this transect one would assume the samples located between both point sources would be located at a closer proximity to this particular point source. Samples collected outside of the Sudbury area take on a signature that represents a mixing between both Xstrata and the U. S point source. This particular transect borders the Midwestern states and therefore is massively influenced by trans boundary pollution during the summer months from prevailing southwestern winds. These results are similar to those of the snowpack sampled along the W-E transect. The samples located between both point sources take on a signature more similar to the U. S. In the snowpack data set, Essar Steel Algoma is able to take on its on signature. This is because the

prevailing winds are not as strong from the SW. Since Essar Steel has a minimal contribution of lead at 194/yr, during the summer months this point source is diluted with transboundary pollution and it not able to retain a distinct signature.

6.4.3 Stem and Whorl Discussion

Separate sections of the lichen were digested individually. The upper section which is called the whorl was separated from the stem of the lichen. A new whorl grows annually, the upper whorl in this case represents Pb emissions during the Vale Inco Smelter shutdown. The stem of the lichen can retain elements for multiple years. Therefore, this section of the plant represents Pb emissions during Vale Inco Smelter operations. Figure 13 illustrates the differences in Pb^{207}/Pb^{206} isotope ratios between the stem and whorl of the lichen along the West-East transect between Sault Ste. Marie and Sudbury.

Figure 13 shows that the Pb^{207}/Pb^{206} isotopic ratio is consistently higher in the whorl than in the stem of the lichen, approximately 0.01.

The lichen that was sampled along the N-S transect underwent the same digestion procedure as the lichen sampled along the W-E transect. The Pb^{208}/Pb^{206} isotope ratios were plotted against the sample locations in table 14. Except for three samples the isotope ratios of the whorl was higher in all cases than in the stem of the plant in both transects. This is consistent with figure 3, which shows that Falconbridge has a higher Pb^{208}/Pb^{206} ratio, which should be prevalent during the Vale Smelter Shutdown.

The US isotopic fingerprint for both isotopic ratios is higher than both the stem and the whorl. In the whorl of the plant it is assumed that there is minimal influence from Vale Inco's

Smelter. Therefore, the Xstrata Falconbridge operations should be the dominant isotope ratio present in the whorl. The difference between the stem and the whorl should approach a fingerprint more representative of the Xstrata Falconbridge Smelter. From previous studies it was found that the US trans boundary pollution has a major Pb impact on Sudbury's fingerprint. Since the whorl of the plant was sampled during the summer months the prevailing winds are coming from the Southwest, South and West. The stem of the plant represents an annual emission which would include prevailing winds from the Southwest in the summer months and snowmelt with transboundary pollution from the North and West in the winter months. This pattern alone would mean that the whorl of the plant would represent a fingerprint more similar to the US than the stem which is an average between prevailing winds. It cannot be deciphered from the stem and the whorl of the plant an individual signature for both Vale Inco and Xstrata Falconbridge Sudbury Operations. The increase in isotope ratios during the shutdown could take on a fingerprint more similar to Xstrata or it could be the transboundary pollution having a larger influence increasing the ratios.

Figure 13 has a fairly steady ratio over the transect including three spikes with increasing size. These three spikes (216, 223, 611) represent samples located around Sault Ste. Marie (Essar Steel, 223), Espanola (Domtar Pulp and Paper Mill, 611) and 216 which has an unknown source or is an outlier. These locations have plants that emit small amounts of Pb emissions that are shown to throw off the typical isotopic signature along the transect when sampled in the immediate vicinity.

Along the South-North Transect samples there is a different trend. Samples take on signatures according to the area they are in. The Timmins area is located a lot higher than the Sudbury and Kapuskasing Area. Because this data set does not border the Midwestern states

there is not as much transboundary pollution and area signatures can be observed. Any samples collected outside of The Timmins Met Plant along this transect are located around 0.88 as seen in Figure 11. The U. S point source is 0.83 therefore most samples sets are created as a result from the blending of the point source in their vicinity and the U. S point source. The Pb^{207}/Pb^{206} isotope ratio for the stem is generally 0.02 or more lower than measured for the lichen whorl, indicative perhaps of the recent lichen growth represented by the whorl material having absorbed the current seasonal lead input, which was isotopically different from that of the previous seasons or from season wind patterns bringing transboundary pollution from the U. S

6.5 Conclusion

Stem and Whorl Studies

It could not be deciphered that the difference in the stem and the whorl approach isotopic signatures that are significantly different from the Vale Inco and Xstrata Falconbridge Smelter Sudbury Operations. This is highly due to the fact the US trans boundary pollution has a major impact on the Sudbury isotopic signature. According to figures 11 and 13, during the shutdown of the Vale Inco Sudbury Smelter the isotopic signature approaches a different fingerprint. This fingerprint may not approach an isotopic ratio more similar to Falconbridge because it is also approaching a fingerprint that related to the US trans boundary fingerprint. The whorl represents summer accumulation during the Vale Smelter shutdown, during this period transboundary prevailing winds are also dominant from the SW. The stem of the plant represents accumulation of airborne pollution form the summer as well as snowmelt from the previous winter. During the winter months there are dominant winds from the North. The whorl therefore would contain more pollution from the Midwestern states.

W-E Transect Bio-monitoring Study

The difference in graphs between the snowpack and the lichen along the W-E Transect was the amount of transboudary pollution. Point sources could be easily deciphered during the winter months because prevailing winds were not predominantly from the SW. During the summer months this transect parallels the mid western states, therefore it is hard to pull out point source polluters expecially Essar Steel Algoma because of the overwhelming transboundary signature on a smaller point source emitter.

N-S Transect Bio-monitoring Study

Samples collected along the S-N transect have distinct isotope signatures relative to their location. Because the graph shows a linear relationship it is unclear whether or not the data sets are a function of influence from their closest point source emitters or a function of distance from the US border. The Kapuskasing data set in purple is located away from major point sources. Because of the SW winds these samples take on direct mixing between the U. S point source and the Kidd |Met Site. Therefore the most northly sample is still directly influences by the SW winds transboundary pollution. A linear relationship does not show a three way distribution therefore it is unclear how much of an influence Sudbury's Xstrata and Vale Operations have on the samples or if it is actually the states.

7.0 Thesis Conclusion

Snowpack samples located along a W-E transect from Sudbury to Sault Ste. Marie and the S-N transect from Sudbury up through Timmins to Kapuskasing resulted in similar trends. Each major northern Ontario point source had a distinct signature that was distinguishable from one another. Samples located in close proximity to these major point sources resembled signatures

that were greatly influenced by these point sources. Samples that were collected between major point sources outside a 10km radius of a major point source had signatures that slightly resembled these major point source signatures but more so resembled the transboundary U. S signature from coal fired power plants. Results showed that snowpack samples that were collected at greater distances from the U. S border show no trends that the U. S signature decreases with distance as proven with the north most snowpack sample (Kapuskasing). Samples that were collected around the Falconbridge and Vale Smelter during operational periods showed differences in isotope signatures. Samples that were collected before and after the Vale Inco Copper Cliff Smelter shutdown did not show differences in isotopic ratios, which may be the case because of dilution with transboundary pollution.

Atmospheric fallout was collected in rainwater during the Copper Cliff Smelter Shutdown. Rainwater was collected between July and December. It is inconclusive whether or not there is an apparent atmospheric washout of Pb from the residual Pb from the Copper Cliff Smelter. As rainfall events approach the winter season the signature gains distance from the U. S fingerprint. This trend may be due to atmospheric washout or from a gradual change in prevailing winds from the SW to North as the seasons change from summer through fall to winter. During the initial sampling period in July the prevailing winds are from the SW. The dominant transboundary pollution at this time creates an overall Sudbury signature that cannot differentiate the Copper Cliff Smelter from the Falconbridge Smelter.

To complete the overall annual sampling of Pb over the entire year Lichen was sampled during the summer months. This sampling period also took place during the Copper Cliff Smelter Shutdown. The sampling transects mimicked that of the snowpack transects. Graphically it was shown that the samples resulted in the same conclusions as the snowpack samples. Again,

with the lichen samples each northern Ontario point source had an isotope signature that could be differentiated from each other. Samples located around these point sources reflected these signatures as well as small contributions from the U.S signature. The U. S signature was more prevalent as distance was gained from the northern Point sources. Point sources were not as clear in the lichen because they were more diluted with transboundary pollution as was seen with Essar Steel, a minor but still significant contributor of Pb pollution.

The stem and whorl approach coincided with the snowpack that was collected during an operational time at the Vale and Falconbridge, Sudbury smelters. There was an overall change in signature during each event but it is inconclusive with this study wither or not Vale and Falconbridge have a distinct signatures from each other or if there is an overall atmospheric dilution of the Sudbury fingerprint and the U.S becomes the prevailing signature.

The Pb isotope fingerprint in northern Ontario can be explained by a binary mixing of anthropogenic emissions from northern Ontario refining operations and coal fired power plant emissions that are transported with prevailing winds from the Ohio Valley.

References

Agency, U. E. (2008). *National Emissions Inventory.* U.S EPA.

Air Quality. (2010, December 20). Retrieved June 14, 2011, from Environment Canada: http://www.ec.gc.ca/indicateurs-indicators/default.asp?lang=En&n=3618F1AA-1

Alian, A. and B. Sansoni (1980). Instrumental neutron activation analysis of geological and pedological samples. Further investigation of epithermal neutron activation analysis using monostandard method. *Radio Analytical Chemistry*, 59: 511-543.

Ames, D., Kjarsgaard, I., & Douglas, S. (2007). Sudbury Ni-Cu-PGE Ore Mineralogy Complilation: Sudbury Targeted Geoscience Initiative.

Andreev, V. (1954). Growth of forage lichens and methods of regulating it. Proceedings of the Komarov Botanical Institute, Series III. *Geobotanika*, 11-74.

Berg, T., & Steinnes, E. (1997). Use of mosses (*Hylocomium splendens and Pleurozium schreberi*) as biomonitors of heavy metal deposition: From relative to absolute deposition values . *Environmental Pollution 98*, 61-71.

Cabri, L. J. (1981). The platinum group minerals. In L. J. Cabri, *Canadian Institute of Mining and Minerology* (pp. 136-138).

Canada, E. (2009, December 30). *Environment Canada*. Retrieved from National Pollution Release Inventory: http://www.ec.gc.ca/inrp-npri/

Carignan j, G. C. (1995). Isotopic composition of epiphytic lichens as a tracer of the sources of atmospheric Pb emissions in southern Quebec, Canada. *Geochimica et Cosmochimica Acta*, 4427-4433.

Chang, H., & Yu, Y. (2009). Lead isotope fingerprinting and its applications in lead pollution studies in China: A Review. *Environmental Pollution*, 1-5.

Church, T. M. (1994). Acidic Deposition. *Fundamentals of Air Pollution 3rd ed*, 149-152.

College, C. (2012). *Concordia College* . Retrieved from Analytical Chemistry Labortory Manual: http://wwwp.cord.edu/dept/chemistry/analyticallabmanual/experiments/icpaes/intro.html

Consulting, P. A. (2004). *Air Quality Trends.* Greater Sudbury.

Consulting, P. A. (2004). *Air Quality Trends City of Greater Sudbury, Ontario 1953-2002.* Sudbury, Ontario.

Cortecci, G., & Longinelli, A. (1970). *Letters to Nature*, 36.

Crook, T. (1921). A practicle guide to the Study of Useful Minerals. *Ecomonic Minerology*.

Doe, B. R. (1970). *Lead Isotopes.* New York: Springer Veriag.

Education, T. J.-O. (2013, September 18). *Isotopes of the Element Lead*. Retrieved september 18, 2013, from Its Elemental: http://education.jlab.org/faq/index.html

Environment Canada. (2010, december 6). *Environment Canada's Gasoline Regulations*. Retrieved June 15, 2011, from Environment Canada: http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=en&n=54fe5535-1&wsdoc=8e3c2e9b-38a8-461a-8ec3-c3aa3b1fd585

Essar Steel. (2011, February 14). *www.algoma.com*. Retrieved December 26, 2011, from http://www.algoma.com/company/environment/air-quality/

Fature, G. (1986). *Principles of Isotope Geology.* New York: Wiley and Sons.

Geiser, L. (2009, December 18). *United States Forest Service*. Retrieved from National Lichens & Air Quality Database and Clearinghouse: http://gis.nacse.org/lichenair/?page=airpollution

Halstead, M., Cunninghame, R., & Hunter, K. (2000). Wet deposition of trace metals to a remote site in Fiordland, New Zealand. *Atmospheric Environment*, 665-676.

Hefa, C., & Yuanan, H. (2010). Lead isotopic fingerprinting and its applications in lead pollution studies in China: A review. *Environmental Pollution*, 2.

Hoffman, E. (1977). Further Consideration of alkali and alkaline earch geochemistry of marine aerosols: results of a study of marine aerosols collected on Bermuda. *Atmospheric Environment*, 373-377.

International, I. (2011). *Coal-Fired Electric Generation Unit Retirement Analysis.* ICF International.

J. Carignan, A. S. (2002). Dispersal of atmospheric lead in northeastern North American as recorded by epiphytic lichens. *Atmospheric Environment*, 3759-3766.

K.J.R, R., Chisholm, W., Boutron, C., Candelone, J., & Patterson, C. (1994). Anthropogenic lead isotopes in Antarctica. *Geophysical Research Letters*, 2669–2672.

Kropschot, S. J. (2011). *Uses of Lead.* Retrieved june 14, 2011, from United States Geological Survey: http://geology.com/usgs/lead/

Laurentian, U. (2003, February 4). *Sudbury Basin Virtual Field Trip*. Retrieved June 16, 2011, from Earth Sciences Laurentian: http://oldwebsite.laurentian.ca/geology/virtual/index.htm

Loppi, S., Ivanov, D., & Boccardi, R. (2002). Biodiversity of epiphytic lichens and air pollution in the town of Siena. *Environmental Pollution*, 123-128.

Mart, L. (1983). Seasonal variations of Cd, Pb, Cu and Ni levels in snow from the eastern Arctic Ocean. In L. Mart, *Tellus B* (pp. 131-141). International Meteorological Institute in Stockholm.

Michelle DesJardins, K. T. (2004). Apportioning atmospheric pollution to Canadian and American sources in Kejimkujik National Park, Nova Scotia, using Pb isotopes in precipitation. *Atmospheric Environment*, 6875-6881.

Morrison, R. D. (2000). Application of Forensic Techniques for Age Dating and Source Identification in Environmental Litigation. *Environmental Forensics*, 131-153.

Negrel, P. (1998). Chemistry of rainwater in Massif Central (France): a strontium isotope and major element study. *Journal of applied geochemistry*, 941-952.

Neymark, L., & Amelin, Y. (2008). Natural radionuclide mobility and its influence on the U-Th-Pb dating of secondary minerals from the unsaturated zone, Yucca Mountain, Nevada. *Geochim. et Cosmochim. Acta*, 2067-2089.

Nriagu, & Coker. (1999). Tracing sources of atmospheric sulphur using epiphytic lichens. *Environmental Pollution*, 165-271.

Nriagu, J., & Coker, R. (1978). Isotopic composition of sulphur in atmospheric precipitation around Sudbury, Ontario. *Letters to Nature*, 883-885.

Nylander, W. (1866). Les Lichens du Sardin du Luxembourge. *Soc. Bot. Fr*, 364-372.

Ontario, M. O. (1994). *Ontario Indistry Emissions Reduction Plan.* Ontario: Ministry of the Environment.

Perez, E. (2011, febuary 2). *Lead Poisioning: Medline Medical Encyclopedia*. Retrieved june 14, 2011, from Medline Plus: http://www.nlm.nih.gov/medlineplus/ency/article/002473.htm

Potvin, R. (1976). Air Quality Assessment Studies in the Sudbury Area. *Ambient Air Quality*.

Ruhling, A., & G, T. (1969). A regional and historical study. In B. Notiser, *Ecology of heavy metals* (pp. 248-259).

SARA Group. (2001). Sudbury Soils Study Volume I: Background, Study Organization and 2001 Soil Survey. SARA Group.

Steinnes, E. (2008). Use of mosses to study atmospheric deposition of trace elements: Contribution from investigations in Norway. *International Journal of Environment and Pollution 32*, p.499.

Sturges, W., & Barrie, L. (1987). *Nature*, 144-146.

Sturm, E. (2011, April 11). *Health Effects of Pollution*. Retrieved June 14, 2011, from U.S Environmental Protection Acency: http://www.epa.gov/region7/air/quality/health.htm

Toms, A. (2005). *Varian Analytical Instruments, Introduction to ICP MS Theory and Practice.* Andrew Toms (presenter).

Ulrich, T. K. (2010). Long-term observations of isotope ratio accuracy and reproducibility using quadrupoe ICP mass spectrometry. *Geostandards and Geoanalytical Research 34*, 161-174.

University, B. (2014, Jan 4). *Nerc Life Sciences*. Retrieved from http://www.bris.ac.uk/nerclsmsf/images/quadrupole.gif

Veron, A., Church, T., Patterson, C., Rel, Y., & Merril, J. T. (1992). Continential Origin and Industrial Sources of Trace metals in the Northwest Atlantic Troposphere. *Atmospheric Chemistry*, 339.

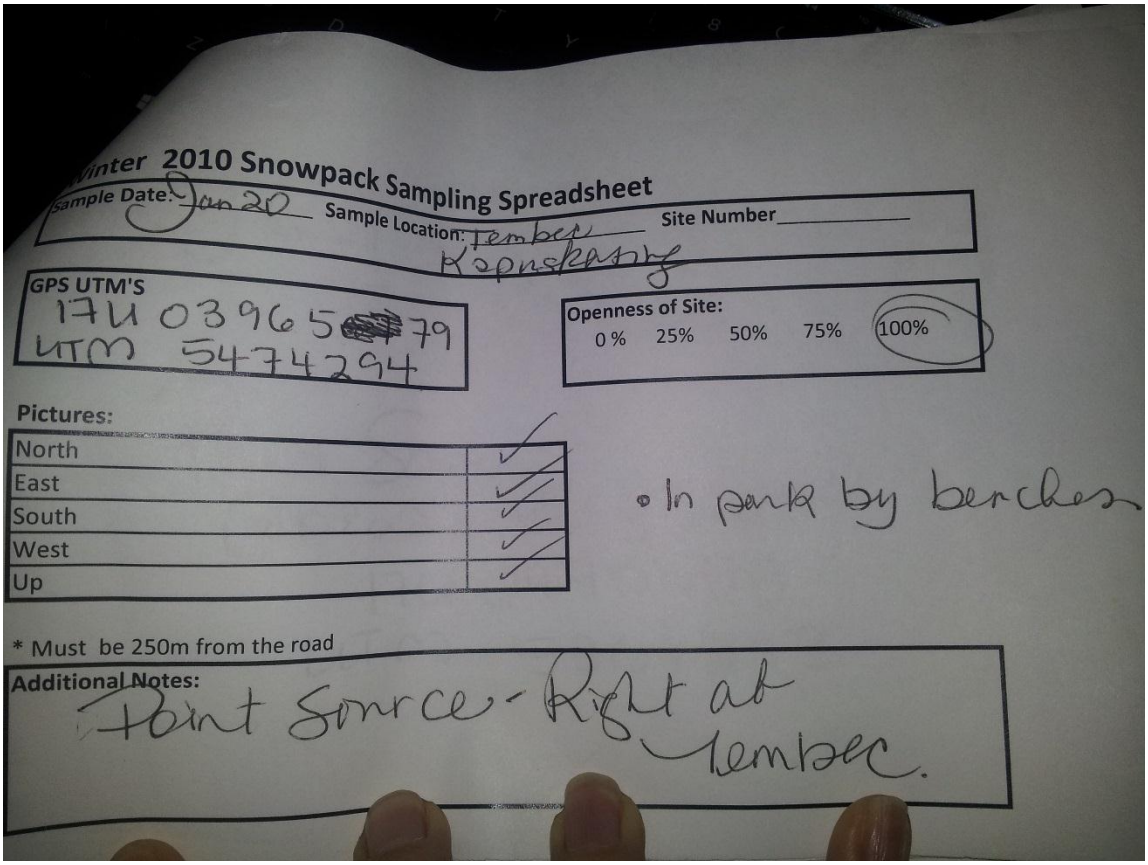
Walter, C. H. (1985). *Air Resources Branch.* Toronto: Ontario Ministry of the Environment.

Xstrata. (2011, Jan 5). *Kidd Operations*. Retrieved June 7, 2011, from Xstrata Nickel:

http://www.xstratacopper.com/EN/Operations/Pages/KiddMine.aspx

APPENDICES

Appendix a. Sample field sheet recorded for every snowpack sample collected



Winter 2010 Snowpack Sampling Spreadsheet

Sample Date: Jan 20 Sample Location: Tembec Kapuskasing Site Number_____

GPS UTM'S
17U 0396579
UTM 5474294

Openness of Site:
0 % 25% 50% 75% 100%

Pictures:

North	✓
East	✓
South	✓
West	✓
Up	✓

* In park by benches

* Must be 250m from the road

Additional Notes:
Point Source - Right at Tembec.

Appendix b. Snowpack data including sample ID, location, GPS units and isotope ratio data.

ID	Location	Lat	Long	^{207}Pb / ^{206}Pb	^{208}Pb / ^{206}Pb	^{206}Pb / ^{204}Pb
1	Searchmont, Sault Ste. Marie	46°41'45.96 "N	84°16'57.73 "W	0.868	2.106	17.898
2	Peoples St. Sault Ste. Marie	46°34'4.52" N	84°21'34.64 "W	0.841	2.054	18.745
3	Essar Steel Sault Ste. Marie	46°31'56.34 "N	84°21'59.21 "W	0.846	2.075	19.090
4	East of Sault Ste. Marie	46°33'13.20 "N	84°10'46.62 "W	0.840	2.054	18.724
5	Browns Island	46°19'49.35 "N	84° 4'4.64"W	0.838	2.050	18.838
6	Off Bear St, Portlock	46°20'27.45 "N	83°53'16.91 "W	0.839	2.055	18.741
7	Lafarge, Bruce Mines	46°20'11.78 "N	83°42'12.38 "W	0.872	2.114	17.854
8	Walford, Thessalon	46°16'54.27 "N	83°29'43.12 "W	0.853	2.082	18.426
9	James St, Iron Bridge	46°16'28.08 "N	83°12'51.58 "W	0.840	2.059	18.677
10	Carmeuse Lime, Blind River	46°11'0.56" N	83° 1'14.15"W	0.833	2.049	18.939
11	Spragge	46°12'24.14 "N	82°39'7.98" W	0.835	2.031	18.993
12	Spanish River	46°11'1.19" N	82°18'40.52 "W	0.844	2.066	18.550
13	Massey	46°13'16.92 "N	82° 2'35.57"W	0.845	2.070	18.519
14	Domtar Pulp and Paper, Espanola	46°17'2.60" N	81°45'53.09 "W	0.845	2.063	18.697
15	Beaver Lake	46°19'53.71 "N	81°28'41.16 "W	0.855	2.086	18.348
16	Penguin Research, Naughton	46°24'6.84" N	81°11'18.58 "W	0.866	2.119	18.070
17	Vale Inco, Copper Cliff	46°28'26.82 "N	81° 4'32.03"W	0.875	2.134	17.871
18	Kelly Lake, South End Sudbury (1)	46°27'27.64 "N	81° 2'0.03"W	0.873	2.122	17.902
19	Kelly Lake, South End Sudbury (2)	46°27'27.64 "N	81° 2'0.03"W	0.882	2.152	17.735
20	Big Nickel, Sudbury(2)	46°28'29.27	81° 1'56.55"W	0.870	2.123	17.966

		"N				
21	Big Nickel, Sudbury(1)	46°28'29.27 "N	81° 1'56.55"W	0.903	2.208	17.259
23	Bell Park, Sudbury(1)	46°28'56.25 "N	80°59'1.13" W	0.879	2.150	17.897
24	Laurentian conservation, Sudbury(2)	46°27'26.14 "N	80°56'30.55 "W	0.853	2.079	18.288
25	Laurentian conservation, Sudbury(1)	46°27'26.14 "N	80°56'30.55 "W	0.912	2.214	16.978
26	Minnow Lake, Sudbury (1)	46°29'9.82" N	80°54'54.46 "W	0.914	2.194	16.878
27	Minnow Lake, Sudbury (2)	46°29'9.82" N	80°54'54.46 "W	0.901	2.191	17.246
28	Vale Inco, Coniston (1)	46°28'38.56 "N	80°51'14.14 "W	0.922	2.209	16.801
29	Vale Inco, Coniston (2)	46°28'38.56 "N	80°51'14.14 "W	0.928	2.236	16.700
30	Xstrata Falconbridge (1)	46°30'12.33 "N	80°49'7.54" W	0.959	2.310	16.068
31	Xstrata Falconbridge (2)	46°30'12.33 "N	80°49'7.54" W	0.917	2.206	16.794
32	Make Rd, Garson (1)	46°32'11.50 "N	80°51'31.77 "W	0.945	2.262	16.342
33	Make Rd, Garson (2)	46°32'11.50 "N	80°51'31.77 "W	0.976	2.306	15.517
34	Hanmer (2)	46°39'23.29 "N	80°56'0.56" W	0.911	2.196	16.910
35	Hanmer (1)	46°39'23.29 "N	80°56'0.56" W	0.877	2.132	17.845
36	Skead	46°39'33.84 "N	80°44'44.36 "W	0.927	2.245	16.644
37	Clarabelle/Lasalle Intersection Sudbury (1)	46°30'19.30 "N	81° 2'35.40"W	0.879	2.147	17.752
38	Clarabelle/Lasalle Intersection Sudbury (2)	46°30'19.30 "N	81° 2'35.40"W	0.889	2.167	17.492
39	Onaping	46°37'31.18 "N	81°25'2.25" W	0.860	2.098	18.210
40	Benny Lake	46°47'51.31 "N	81°35'57.39 "W	0.856	2.090	18.412
41	Gogama	46°57'1.50" N	81°50'40.73 "W	0.869	2.115	17.802
42	Cutover	47° 6'32.29"N	81°41'42.18 "W	0.876	2.119	17.791
43	Big Truck	47°19'53.05 "N	81°46'20.21 "W	0.869	2.109	18.060

44	Kenetogami	47°44'58.25 "N	81°39'56.67 "W	0.854	2.082	18.416
45	Matagami Lk,	47°58'4.74" N	81°35'49.40 "W	0.862	2.097	18.243
46	McKeowen	48°13'44.02 "N	81°33'40.35 "W	0.858	2.089	18.146
47	Halfway to Luzenac Pentahorwood	48°14'38.75 "N	81°50'29.62 "W	0.944	2.245	15.934
48	Luzenac Pentahorwood Point Source	48°12'55.19 "N	82° 5'9.98"W	0.868	2.102	18.082
49	Outside Montcalm Mine	48°25'40.24 "N	81°28'4.51" W	0.899	2.159	17.192
50	Montcalm Rd.	48°27'2.52" N	81°33'11.76 "W	0.886	2.140	17.631
50 b	Luzenac Micronizing Plant	48°28'34.79 "N	81°18'57.08 "W	0.917	2.194	16.938
51	Xstrata Montcalm Mine	48°30'58.69 "N	81°22'45.61 "W	0.885	2.143	17.635
52	Big Water	48°32'52.80 "N	81°16'24.12 "W	0.977	2.299	15.339
53	Kidd Met Site Xstrata	48°32'38.39 "N	81° 4'28.23"W	1.020	2.378	14.547
54	Goldcorp Dome Site	48°32'38.46 "N	81° 4'28.07"W	0.898	2.163	17.162
55	Kidd Mine Site Xstrata	48°40'42.45 "N	81°21'36.76 "W	1.005	2.348	14.919
56	Black Pearl	48°45'11.05 "N	81°21'25.80 "W	0.898	2.159	17.229
57	Tembec Kapuskasing	49°24'45.11 "N	82°25'32.87 "W	0.871	2.097	18.365

Appendix c. Quality Control Data for NBS 982 during the snowpack analysis in appendix B.

Standard	Pb207/Pb206 0.46707 (certified value)	Pb208/Pb206 1.00016 (certified value)	Pb206/Pb204 36.74432 (certified value)
NBS 982 a	0.46668	1.00092	36.740
NBS 982 b	0.46732	0.99927	36.811
NBS 982 c	0.46685	0.99983	36.763
NBS 982 d	0.46719	1.00094	36.667
NBS 982 e	0.46709	1.00071	36.653
NBS 982 f	0.46675	0.99898	36.757
NBS 982 g	0.46675	0.99972	36.696
average	**0.46695**	**1.00005**	**36.727**
stdev	**0.00025**	**0.00081**	**0.057**
rsd	**0.054**	**0.081**	**0.155**

Appendix d. ICP MS raw sample data (counts) for lichen sample run

Sample ID	Pb204	Pb206	Pb207	Pb208
2% nitric	37.302	720.143	578.500	1373.750
SRM 982	38854.375	1403433.500	651046.188	1379501.000
2% Nitric Blank	38.171	612.000	487.667	1130.444
Digestion Blank 1a	251.278	4521.400	3798.714	9118.000
Digestion SRM 982 (1a)	54686.930	1978044.000	920686.000	1954287.250
411(s1)	14540.938	262275.688	219858.906	534008.000
411(s2)	14267.215	256471.797	215973.906	524076.406
411(s3)	14890.354	267927.000	224384.000	545345.875
AVG	14566.169	262224.828	220072.271	534476.760
STD	312.335	5727.771	4209.105	10642.480
%RSD	2.144	2.184	1.913	1.991
2% Nitric Blank	12617.282	337534.074	201052.498	457009.690
411(w1)	8095.577	143686.094	121421.297	294917.906
411(w3)	8140.353	146205.297	123282.703	298335.906
AVG	8117.965	144945.695	122352.000	296626.906
STD	31.661	1781.346	1316.213	2416.891
%RSD	0.390	1.229	1.076	0.815
622(s1)	19990.479	347896.188	299632.000	718225.500
622(s2)	19974.643	345909.000	297225.500	712653.125
622(s3)	19862.363	346147.813	297657.000	713355.688
AVG	19942.495	346651.000	298171.500	714744.771
STDEV	69.846	1084.955	1283.099	3034.799
%RSD	0.350	0.313	0.430	0.425
2% Nitric Blank	15.832	334.750	293.571	666.600
SRM 981	38155.246	633733.813	572086.000	1334110.000
SRM 982	38581.016	1385927.125	641115.813	1350481.000
2% Nitric Blank	28.062	102.000	89.571	169.889
622(s1)	19974.643	345909.000	297225.500	712653.125
622(s2)	19862.363	346147.813	297657.000	713355.688
622(s3)	19974.643	345909.000	297225.500	712653.125
AVG	19942.495	346651.000	298171.500	714744.771
STDEV	69.846	1084.955	1283.099	3034.799
%RSD	0.350	0.313	0.430	0.425
622(w1)	17348.361	300359.688	259216.406	620531.375
622(w2)	20098.898	347196.688	300684.000	719018.188
622(w3)	20048.934	346556.111	299656.222	716560.111
AVG	19165.398	331370.829	286518.876	685369.891
STDEV	1573.798	26858.346	23650.216	56165.251

%RSD	8.212	8.105	8.254	8.195
2% nitric	45.064	301.300	267.500	575.875
141(s1)	12141.405	197944.594	176932.203	419291.688
141(s2)	11059.499	182282.406	163212.906	386402.594
141(s3)	11079.182	181725.556	162610.444	384061.222
AVG	11426.695	187317.519	167585.185	396585.168
STDEV	619.035	9207.528	8100.358	19699.239
%RSD	5.417	4.915	4.834	4.967
141(w2)	7293.084	119285.900	107258.200	253239.400
141(w3)	7223.110	116716.602	105515.297	248515.406
AVG	7258.097	118001.251	106386.748	250877.403
STDEV	49.479	1816.768	1232.419	3340.368
%RSD	0.682	1.540	1.158	1.331
2% rinse	52.972	363.900	331.400	750.800
SRM 981	38331.867	638852.375	577343.813	1350132.750
SRM 982	33095.426	1188746.250	550198.313	1161385.500
2%nitric	53.431	495.375	419.625	939.444
310(s1)	40043.531	650182.188	590524.313	1393302.250
310(s2)	40136.578	643550.625	587064.000	1384441.375
AVG	40090.055	646866.406	588794.156	1388871.813
STDEV	65.794	4689.223	2446.810	6265.585
%RSD	0.164	0.725	0.416	0.451
310(w1)	23154.264	377972.500	342056.500	806636.375
310(w2)	22609.166	365050.000	331230.188	782152.188
310(w3)	23939.721	391632.906	353019.313	833931.188
AVG	23234.383	378218.469	342102.000	807573.250
STDEV	668.886	13293.160	10894.634	25902.211
%RSD	2.879	3.515	3.185	3.207
2% nitric	16810.974	316887.048	252236.344	585174.203
Digestion blank 2a	283.411	4676.400	4010.100	9556.200
Digestion SRM 982 2a	17612.578	332150.986	263666.660	612409.016
2% nitric	16580.388	275044.635	244564.549	575810.584
SRM 981	40196.371	668588.500	604252.313	1409969.875
SRM 982	34849.457	1255119.750	577691.125	1221330.875
2% nitric	17339.899	335346.282	261131.219	604372.468
610(s1)	18252.490	362614.165	275912.164	636524.741
610(s2)	20542.938	370937.813	310879.500	750993.625
610(s3)	20092.584	364237.500	304871.313	736484.875
AVG	20317.761	367587.656	307875.406	743739.250
STDEV	318.448	4737.836	4248.430	10259.236
%RSD	1.567	1.289	1.380	1.379

2% nitric	20638.902	440968.448	316330.994	728605.807
610(w1)	13333.065	240377.094	201911.594	487045.906
610(w2)	14253.837	256624.703	215785.297	520611.406
610(w3)	12994.960	235151.906	197662.297	476560.406
AVG	13527.287	244051.234	205119.729	494739.240
STDEV	651.525	11197.979	9477.863	23011.153
%RSD	4.816	4.588	4.621	4.651
311(s1)	11375.021	187297.000	167763.297	404764.406
311(s2)	11595.470	187164.203	169370.406	403208.406
AVG	11485.245	187230.602	168566.852	403986.406
STDEV	155.881	93.902	1136.398	1100.258
%RSD	1.357	0.050	0.674	0.272
2% rinse	12202.536	225518.731	184271.594	438807.935
SRM 981	38657.578	642423.375	580589.125	1358864.250
SRM 982	34603.227	1242164.875	574066.313	1212069.125
2% rinse	12432.161	254570.156	189950.188	444413.914
311(s3)	13206.581	218105.500	195441.000	465887.594
311(w1)	8281.305	131384.594	121101.297	285120.688
311(w2)	9072.457			
311(w3)	8766.645	138886.797	128550.703	302519.188
AVG	8706.802	135135.695	124826.000	293819.938
STDEV	398.957	5304.859	5267.526	12302.597
%RSD	4.582	3.926	4.220	4.187
2% rinse	11352.209	230456.936	172478.788	399456.523
203(s1)	8302.125	149494.203	125961.102	305583.094
203(s2)	8054.494	144703.797	121943.898	295697.094
203(S3)	8934.091	160670.094	135557.094	328786.000
AVG	8430.236	151622.698	127820.698	310022.063
STDEV	453.577	8193.200	6994.523	16985.207
%RSD	5.380	5.404	5.472	5.479
203(w1)	5989.634	106560.000	90410.797	218424.906
203(w2)	6012.063	107293.297	90808.797	219236.406
203(w3)	5968.345	106595.297	90224.000	217954.297
AVG	5990.014	106816.198	90481.198	218538.536
STDEV	21.861	413.557	298.687	648.564
%RSD	0.365	0.387	0.330	0.297
2% rinse	6911.054	120557.942	103437.662	246473.427
SRM 981	24482.457	405587.094	366765.188	853370.375
SRM 982	22375.320	800523.625	368174.094	775889.813
2% nitric	10838.179	233244.228	166576.142	386087.193
307(s1)	48097.996	745305.375	699386.313	1637577.375

307(s2)	45694.168	700661.125	660778.813	1547755.250
307(s3)	47739.910	738038.313	695833.375	1627190.625
AVG	47177.358	728001.604	685332.833	1604174.417
STDEV	1296.899	23954.726	21338.482	49135.658
%RSD	2.749	3.290	3.114	3.063
307(w1)	21065.230	341028.406	309519.813	778471.500
307(w2)	19672.938	305861.813	287091.188	671829.625
307(w3)	19136.670	295653.188	278651.500	650521.813
AVG	19958.279	314181.135	291754.167	700274.313
STDEV	995.440	23804.117	15953.705	68553.671
%RSD	4.988	7.577	5.468	9.790
2% nitric	25284.560	449740.322	374778.658	874259.948
Digestion blank 3a	1199.253	20854.301	17943.600	42903.602
Digestion SRM 982 3a	67907.703	2447930.000	1131688.875	2392409.750
2%nitric	30663.661	627831.707	462224.827	1060900.668
SRM 981	36029.875	600296.375	542308.625	1266857.000
SRm 982	30498.145	1095070.875	505409.594	1063928.125
2% nitric	29919.794	692230.530	460545.005	1042927.266
222(s1)	13441.264	244902.500	203746.203	491888.313
222(s2)	12303.668	222079.703	184754.500	445242.906
222(s3)	14259.176	259701.797	216083.594	521268.188
AVG	13334.702	242228.000	201528.099	486133.135
STDEV	982.099	18953.105	15781.889	38338.002
%RSD	7.365	7.824	7.831	7.886
222(w1)	8267.891	148799.906	124705.500	300582.500
222(w2)	6852.995	123685.203	103659.000	249901.000
222(w3)	6474.208	117389.500	98564.297	237277.406
AVG	7198.364	129958.203	108976.266	262586.969
STDEV	945.402	16618.252	13858.052	33504.986
%RSD	13.134	12.787	12.717	12.760
2% rinse	31.078	198.600	178.286	368.600
216(s1)	10609.650	202343.000	163029.000	391695.500
216(s2)	10040.896	193526.406	154430.406	371209.813
AVG	10325.273	197934.703	158729.703	381452.656
STDEV	402.170	6234.273	6080.124	14485.569
%RSD	3.895	3.150	3.830	3.797
216(w1)	9426.077	172137.797	143056.703	344359.406
2% nitric	40.348	277.625	238.333	515.667
SRM 981	33487.164	558149.688	504404.094	1175186.250
SRM 982	29183.635	1051032.125	485820.594	1026280.500
2% nitric	48.408	452.444	374.333	815.429

216(w1)	9426.077	172137.797	143056.703	344359.406
216(w2)	8759.617	160265.594	133079.594	320227.906
216(w3)	9884.634	181681.500	150288.906	361293.688
AVG	9356.776	171361.630	142141.734	341960.333
STDEV	565.701	10729.030	8641.064	20637.739
%RSD	6.046	6.261	6.079	6.035
223(s1)	15343.106	305735.594	237857.500	587015.188
223(s2)	14834.258	301729.188	231139.500	575336.375
223(s3)	14324.215	290901.094	223019.797	553778.375
AVG	14833.860	299455.292	230672.266	572043.313
STDEV	509.446	7674.213	7429.878	16861.335
%RSD	3.434	2.563	3.221	2.948
2% nitric	67.932	798.286	693.111	1639.800
223(w1)	10735.579	210295.297	165318.000	405638.813
223(w2)	10860.800	212906.797	167379.906	411025.406
AVG	10798.189	211601.047	166348.953	408332.109
STDEV	88.544	1846.609	1457.988	3808.897
%RSD	0.820	0.873	0.876	0.933
404(s1)	12377.246	221853.406	188251.703	456716.406
404(s2)	11942.210	214291.703	181903.594	441335.594
404(S3)	12404.968	222040.406	188839.406	458205.188
AVG	12241.475	219395.172	186331.568	452085.729
STD	259.541	4420.722	3845.980	9339.603
%RSD	2.120	2.015	2.064	2.066
2% rinse	25.088	88.286	80.875	144.571
SRM 981	35951.473	596885.875	540217.813	1260234.250
SRM 982	28553.717	1025192.500	473044.188	997966.625
2% rinse	29.791	106.500	90.833	166.833
404(w1)	10021.123	175877.594	149987.906	362607.406
404(w2)	10225.617	178422.406	152643.594	369422.094
AVG	10123.370	177150.000	151315.750	366014.750
STDEV	144.599	1799.454	1877.855	4818.712
%RSD	1.428	1.016	1.241	1.317
Digestion blank 4	369.807	5952.300	5237.400	12397.900
Digestion SRM 4	74464.563	2680297.750	1238180.125	2613465.500
2% rinse	30.230	169.333	122.800	259.875
306(S2)	45297.957	700627.500	661226.125	1548412.750
306(S3)	39562.902	607565.875	572974.813	1337962.875
AVG	42430.430	654096.688	617100.469	1443187.813
STDEV	4055.296	65804.506	62403.102	148810.534
%RSD	9.558	10.060	10.112	10.311

306(W1)	22811.563	350331.094	331394.594	774133.500
306(w2)	21785.785	333409.313	315094.188	735978.375
AVG	22298.674	341870.203	323244.391	755055.938
STDEV	725.334	11965.506	11526.128	26979.748
%RSD	3.253	3.500	3.566	3.573
2% nitric	34.777	164.333	149.000	288.111
SRM 981	38738.930	645844.188	584444.875	1361546.000
SRM 982	33337.781	1200733.250	553983.625	1168450.250
2% nitric	24.505	109.000	92.800	152.286
405(s2)	35350.992	635030.375	535276.688	1296630.375
405(s3)	33315.316	599316.125	504658.813	1224093.875
AVG	34333.154	617173.250	519967.750	1260362.125
STDEV	1439.440	25253.788	21650.107	51291.051
%RSD	4.193	4.092	4.164	4.070
405(w1)	26233.008	471080.313	398233.688	964260.000
405(w2)	23768.355	426075.594	360531.188	873437.313
405(w3)	24602.982	442277.094	373399.813	906842.875
AVG	24868.115	446477.667	377388.229	914846.729
STDEV	1253.535	22794.512	19165.078	45937.309
%RSD	5.041	5.105	5.078	5.021
2% nitric	36.813	217.222	192.300	395.000
405(w3)	24602.982	442277.094	373399.813	906842.875
406(s1)	20098.705	360002.406	305178.000	742472.000
406(s3)	18597.385	334002.094	282648.688	688490.500
AVG	19348.045	347002.250	293913.344	715481.250
SYDEV	1061.594	18384.997	15930.630	38170.685
%RSD	5.487	5.298	5.420	5.335
406(w1)	12888.470	228349.297	195047.203	472587.406
406(w3)	11411.294	203717.703	173432.109	421875.094
AVG	12149.882	216033.500	184239.656	447231.250
STDEV	1044.521	17417.167	15284.179	35859.020
%RSD	8.597	8.062	8.296	8.018
2% nitric	34.835	299.333	262.200	574.900
202(s1)	36711.105	664404.625	555955.625	1347279.250
202(s2)	34353.055	624307.188	522775.688	1267173.000
202(s3)	39532.328	717979.125	600093.813	1451664.000
AVG	36865.496	668896.979	559608.375	1355372.083
STDEV	2593.086	46997.275	38788.272	92511.365
%RSD	7.034	7.026	6.931	6.826
2% nitric	40.369	342.750	298.375	687.300
SRM 981	36967.953	616056.500	557959.625	1303562.750

SRM 982	32231.906	1157808.250	532829.000	1123923.750
2% nitric	49.628	385.667	313.875	713.778
202(w1)	25659.135	464429.594	389023.188	940445.500
202(w2)	24041.893	435603.906	363845.688	881011.375
AVG	24850.514	450016.750	376434.438	910728.438
STDEV	1143.563	20382.839	17803.181	42026.273
%RSD	4.602	4.529	4.729	4.615
Digestion blank 5	23.363	68.000	62.857	102.167
Digestion SRM 5	74068.320	2669353.250	1237327.500	2616287.000
2% nitric	35.224	265.667	210.889	467.000
120(s1)	13069.203	239292.500	199158.000	480495.000
120(s2)	14037.271	255397.594	213136.703	515431.406
120(s3)	14733.542	269568.688	224225.000	542294.375
AVG	13946.672	254752.927	212173.234	512740.260
STDEV	835.860	15148.385	12561.243	30987.455
%RSD	5.993	5.946	5.920	6.043
120(w1)	12675.607	232179.906	193085.109	466402.406
120(w2)	13567.535	248371.500	206521.000	499499.094
120(w3)	13438.914	245902.797	204839.406	495124.500
AVG	13227.352	242151.401	201481.839	487008.667
STDEV	482.133	8723.340	7320.228	17979.092
%RSD	3.645	3.602	3.633	3.692
2% nitric	66.483	912.000	752.000	1776.000
SRM 981	30935.961	516321.406	468201.313	1093068.250
SRM 982	32786.109	1184373.750	548164.000	1156642.125
2% nitric	42.376	324.857	276.900	627.000
240(s1)	9954.160	183668.000	152204.406	369020.313
240(s3)	10899.369	200904.906	166354.703	402671.313
AVG	10426.765	192286.453	159279.555	385845.813
STDEV	668.364	12188.333	10005.771	23794.850
%RSD	6.410	6.339	6.282	6.167
240(w1)	6551.954	117497.398	97835.297	236187.703
240(w2)	5932.262	108507.898	90478.602	219031.000
AVG	6242.108	113002.648	94156.949	227609.352
STDEV	438.188	6356.536	5201.969	12131.621
%RSD	7.020	5.625	5.525	5.330
2% nitric	46.991	350.000	310.286	688.000
116(s1)	22540.455	411151.594	343342.594	831306.188
116(s2)	25503.500	466295.094	388701.688	941337.625
116(s3)	24441.926	445950.906	372163.813	900972.313
AVG	24161.960	441132.531	368069.365	891205.375

STDEV	1501.231	27885.730	22955.070	55662.143
%RSD	6.213	6.321	6.237	6.246
SRM 981	36575.246	609827.625	553088.000	1292103.000
SRM 982	30404.836	1101844.125	510267.813	1076577.250
2% nitric	45.025	442.444	373.375	845.800
116(w1)	10193.730	186821.500	155687.406	376783.313
116(w2)	10676.956	194982.406	162988.797	393404.188
116(w3)	11094.666	202190.406	168774.297	408196.500
AVG	10655.118	194664.771	162483.500	392794.667
STDEV	450.865	7689.375	6558.061	15715.461
%RSD	4.231	3.950	4.036	4.001
402(s1)	20242.555	363828.313	308984.500	753089.000
402(s2)	19568.402	351295.688	298121.094	727711.000
402(s3)	19072.443	342177.406	290271.594	708046.375
AVG	19627.800	352433.802	299125.729	729615.458
STDEV	587.313	10870.231	9396.818	22581.624
%RSD	2.992	3.084	3.141	3.095
2% nitric	39.438	501.300	433.500	962.100
402(w1)	15260.516	272431.094	231889.000	564384.375
402(w2)	14241.512	254401.094	216827.797	527660.625
402(w3)	15361.198	275078.313	233969.563	569256.313
AVG	14954.409	267303.500	227562.120	553767.104
STDEV	619.436	11251.933	9354.221	22739.726
%RSD	4.142	4.209	4.111	4.106
Digestion Blank 6	237.776	3958.400	3402.100	8148.600
Digestion SRM 6	70955.117	2565402.250	1189721.250	2520907.500
2% nitric	57.988	527.625	452.167	1050.333
SRM 981	30165.762	503574.406	453443.313	1057868.875
SRM 982	26841.867	949842.375	443654.500	936026.500
2% nitric	31.582	137.833	110.400	211.714
101(s1)	10158.675	185862.797	153923.500	371625.406
101(s2)	10030.308	183351.406	151839.000	367337.813
101(s3)	10008.507	182943.797	151297.703	365663.094
AVG	10065.830	184052.667	152353.401	368208.771
STDEV	81.142	1580.811	1386.419	3075.097
%RSD	0.806	0.859	0.910	0.835
101(w1)	10176.344	185036.500	153681.406	370987.688
101(w2)	10381.976	189037.594	157137.703	377827.094
101(w3)	9261.589	168595.000	140702.797	339385.688
AVG	9939.969	180889.698	150507.302	362733.490
STDEV	596.424	10833.831	8665.030	20506.932

%RSD	6.000	5.989	5.757	5.653
2% nitric	37.898	134.714	121.286	234.375
217(s1)	15393.762	286051.594	234295.094	566104.375
217(s2)	14558.128	270147.906	221079.406	533016.188
217(s3)	13153.135	243994.406	199927.797	483219.688
AVG	14368.341	266731.302	218434.099	527446.750
STDEV	1132.306	21235.740	17335.686	41722.078
%RSD	7.881	7.961	7.936	7.910
2% nitric	29.475	150.000	145.600	276.500
SRM 981	33342.742	553514.875	501438.313	1167643.375
SRM 982	28695.078	1031452.625	474926.188	1001352.625
2% nitric	37.146	189.000	158.300	313.000
217(w1)	13525.352	247946.297	205813.094	496394.906
217(w2)	13909.490	254538.703	210880.297	508858.906
AVG	13717.421	251242.500	208346.695	502626.906
STDEV	271.627	4661.535	3583.054	8813.379
%RSD	1.980	1.855	1.720	1.753
212(s1)	10383.272	188504.297	156884.500	377535.188
212(s1)	10794.801	196836.797	163785.094	394810.500
212(s3)	11439.048	208041.406	172585.406	416815.500
AVG	10872.374	197794.167	164418.333	396387.063
STDEV	532.145	9803.677	7869.584	19687.557
%RSD	4.894	4.957	4.786	4.967
2% nitric	38.950	222.000	201.000	407.500
212(w1)	5932.671	106427.500	88867.703	214182.906
212(w2)	5319.425	96849.102	80811.203	195249.203
212(w3)	5940.568	108231.203	90352.000	218009.203
AVG	5730.888	103835.935	86676.969	209147.104
STDEV	356.359	6117.615	5133.828	12187.037
%RSD	6.218	5.892	5.923	5.827
140(s1)	7516.994	129963.297	112305.398	268739.406
140(S3)	7952.616	137861.203	119158.500	284428.906
AVG	7734.805	133912.250	115731.949	276584.156
STDEV	308.031	5584.663	4845.875	11094.152
%RSD	3.982	4.170	4.187	4.011
2% nitric	31.465	207.222	173.125	372.700
SRM 981	35149.930	584546.375	528010.125	1234228.875
SRM 982	30185.031	1088900.375	504123.188	1064645.125
2% nitric	30.486	82.222	70.500	115.250
140(w1)	5993.236	103362.297	89580.203	213950.406
140(w3)	6316.883	108212.000	94023.398	224746.797

AVG	6155.060	105787.148	91801.801	219348.602
STDEV	228.853	3429.258	3141.814	7634.201
%RSD	3.718	3.242	3.422	3.480
Digestion blank 7	237.939	3797.750	3297.000	7815.400
Digestion SRM 7	77930.289	2812086.750	1306063.000	2766087.250
2% nitric	38.397	270.300	230.400	492.900
139(s1)	15184.168	264395.188	228618.406	548715.688
139(s2)	16066.088	277957.000	240266.703	574508.000
AVG	15625.128	271176.094	234442.555	561611.844
STDEV	623.612	9589.650	8236.590	18237.919
%RSD	3.991	3.536	3.513	3.247
139(w1)	8844.332	154204.703	132924.000	317804.094
139(w2)	8836.124	154280.406	132973.703	318408.000
AVG	8840.228	154242.555	132948.852	318106.047
STDEV	5.804	53.530	35.145	427.026
%RSD	0.066	0.035	0.026	0.134
2% nitric	36.448	332.444	289.500	625.333
SRM 981	38980.023	651217.188	589536.875	1380856.750
SRM 982	33159.961	1198593.750	553282.688	1172077.875
2% nitric	39.587	315.857	255.833	548.000
139(w3)	9016.627	157016.594	135046.406	324051.906
611(s1)	15846.720	333593.594	248641.406	637000.625
611(s2)	16145.659	344803.000	255462.906	656570.688
611(s3)	15480.738	328927.406	244601.000	626628.250
AVG	15824.372	335774.667	249568.438	640066.521
STDEV	333.023	8159.438	5489.972	15204.841
%RSD	2.104	2.430	2.200	2.376
2% nitric	44.265	292.500	251.100	554.400
611(w1)	9490.619	192035.703	147756.703	372273.000
611(w2)	9546.836	194213.203	149190.781	378257.406
AVG	9518.728	193124.453	148473.742	375265.203
STDEV	39.751	1539.725	1014.046	4231.614
%RSD	0.418	0.797	0.683	1.128
226(s1)	20129.709	369644.094	307841.188	743930.688
226(s2)	18438.484	337661.594	282068.188	682742.813
226(s3)	17143.678	314731.906	261782.406	632881.125
AVG	18570.624	340679.198	283897.260	686518.208
STDEV	1497.395	27580.184	23083.803	55620.963
%RSD	8.063	8.096	8.131	8.102
2% nitric	36.350	309.429	255.571	576.667
SRM 981	36218.691	606201.125	547810.875	1282054.250

SRM 982	30721.432	1105421.600	512130.900	1082613.200
2% nitric	44.014	335.889	278.000	615.400
226(w1)	16582.092	303897.500	253015.906	611494.313
226(w3)	16843.303	309008.906	257127.297	621855.375
AVG	16712.697	306453.203	255071.602	616674.844
STDEV	184.704	3614.310	2907.192	7326.378
%RSD	1.105	1.179	1.140	1.188
Digestion blank 8	218.470	3469.000	2971.800	7036.600
Digestion SRM 8	69887.109	2531126.000	1174844.375	2490321.000
2% nitric	44.209	380.500	325.444	735.800
224(s1)	17444.463	320478.500	266864.594	646826.313
224(s3)	16010.568	293413.313	244631.797	593336.313
AVG	16727.516	306945.906	255748.195	620081.313
STDEV	1013.917	19137.978	15720.961	37823.142
%RSD	6.061	6.235	6.147	6.100
224(w1)	16482.434	303039.813	251985.406	611592.813
224(w3)	17453.119	319632.594	265938.906	644333.375
AVG	16967.776	311336.203	258962.156	627963.094
STDEV	686.378	11732.868	9866.614	23151.074
%RSD	4.045	3.769	3.810	3.687
2% nitric	50.401	494.500	463.889	1057.700

Appendix e. ICP MS Isotope ratios of Lichen with sample location, gps coordinated and sample number

Sample ID (Average)	Location	GPS Coordinates Latitude	GPS Coordinates Longitude	Blank Corrected Pb204 (Counts)	Blank Corrected Pb06 (Counts)	Blank Corrected Pb207 (Counts)	Blank Corrected Pb208 (Counts)
411 stem	North of Cartier, Division Lake	46° 42' 38.22"	81° 33' 42.19"	14314.891	261612.828	216273.557	525358.760
411 whorl	North of Cartier, Division Lake	46° 42' 38.22"	81° 33' 42.19"	7866.687	140424.295	118553.286	287508.906
622 stem	North-east of Westree	47° 29' 13.75"	81° 24' 14.88"	19691.217	342129.600	294372.786	705626.771
622 whorl	North-east of Westree	47° 29' 13.75"	81° 24' 14.88"	18914.120	326849.429	282720.162	676251.891
141 stem	Greenwater Provincial Park	49° 12' 38.62"	81° 17' 32.81"	11175.418	182796.119	163786.470	387467.168
141 whorl	Greenwater Provincial Park	49° 12' 38.62"	81° 17' 32.81"	7006.819	113479.851	102588.034	241759.403
310 stem	South of Timmins	48° 22' 51.17"	81° 18' 55.5"	39838.777	642345.006	584995.442	1379753.813
310 whorl	South of Timmins	48° 22' 51.17"	81° 18' 55.5"	22983.106	373697.069	338303.286	798455.250
610 stem	North of Webbwood	46° 16' 34.64"	81° 53' 46.3"	20034.350	362911.256	303865.306	734183.050
610 whorl	North of Webbwood	46° 16' 34.64"	81° 53' 46.3"	13243.877	239374.834	201109.629	485183.039
311 stem	Coming into Timmins	48° 19' 2.38"	81° 18' 43.85"	11201.834	182554.202	164556.751	394430.206
311 whorl	Coming into Timmins	48° 19' 2.38"	81° 18' 43.85"	8423.391	130459.295	120815.900	284263.737
203 stem	Kiosk	46° 5' 38.9"	78° 53' 8.61"	8146.826	146946.298	123810.598	300465.862
203 whorl	Kiosk	46° 5' 38.9"	78° 53' 8.61"	5706.603	102139.798	86471.098	208982.336
307 stem	North of Timmins, Hersey Lake trails	48° 31' 1.18"	81° 17' 6.71"	46893.947	723325.204	681322.733	1594618.216
307 whorl	North of Timmins, Hersey Lake trails	48° 31' 1.18"	81° 17' 6.71"	19674.868	309504.736	287744.067	690718.112
222 stem	North-east of Sault Ste. Marie	46° 33' 10.78"	84° 12' 26.34"	12135.449	221373.699	183584.499	443229.534
222 whorl	North-east of Sault Ste. Marie	46° 33' 10.78"	84° 12' 26.34"	5999.111	109103.902	91032.666	219683.367
216 stem	North of Glendale	46° 46' 18.52"	84° 2' 26.49"	9126.020	177080.402	140786.104	338549.055
216 whorl	North of Glendale	46° 46' 18.52"	84° 2' 26.49"	8157.523	150507.329	124198.135	299056.732
223 stem	South-east of Echo Bay	46° 27' 22.58"	83° 59' 32.44"	13634.607	278600.991	212728.666	529139.711
223 whorl	South-east of Echo Bay	46° 27' 22.58"	83° 59' 32.44"	9598.936	190746.746	148405.354	365428.508
404 stem	West of Whitefish	46° 24' 27.55"	81° 28' 23.24"	11042.222	198540.871	168387.968	409182.128
404 whorl	West of Whitefish	46° 24' 27.55"	81° 28' 23.24"	8924.117	156295.699	133372.150	323111.148
306 stem	North of Timmins, off of Big Water lake	48° 36' 12.27"	81° 17' 27.9"	42060.622	648144.388	611863.069	1430789.912
306 whorl	North of Timmins, off of Big Water lake	48° 36' 12.27"	81° 17' 27.9"	21928.866	335917.903	318006.991	742658.037
405 stem	North-west of Whitefish	46° 27' 54.2"	81° 27' 34.91"	33963.347	611220.950	514730.350	1247964.225
405 whorl	North-west of Whitefish	46° 27' 54.2"	81° 27' 34.91"	24498.308	440525.367	372150.829	902448.829

406 stem	North-west of Azilda	46° 35' 29.32"	81° 22' 46.72"	18978.238	341049.950	288675.944	703083.350
406 whorl	North-west of Azilda	46° 35' 29.32"	81° 22' 46.72"	11780.074	210081.200	179002.256	434833.350
202 stem	North of Bonfield off Hwy 17	46° 15' 5.56"	79° 10' 52.62"	36495.689	662944.679	554370.975	1342974.183
202 whorl	North of Bonfield off Hwy 18	46° 15' 5.56"	79° 10' 52.62"	24480.706	444064.450	371197.038	898330.537
120 stem	South of Wawa off Hwy 17	47° 56' 13.19"	84° 47' 8.02"	13923.310	254684.927	212110.377	568287.286
120 whorl	South of Wawa off Hwy 18	47° 56' 13.19"	84° 47' 8.02"	13203.990	242083.401	201418.981	486906.500
240 stem	South of Eliot Lake	46° 17' 3.69"	82° 34' 20.89"	10403.402	192218.453	159216.698	385743.646
240 whorl	South of Eliot Lake	46° 17' 3.69"	82° 34' 20.89"	6218.745	112934.648	94094.092	227507.185
116 stem	North end of Lake Superior Provincial Park	47° 45' 29.64"	84° 49' 15.11"	24138.598	441064.531	368006.507	891103.208
116 whorl	North end of Lake Superior Provincial Park	47° 45' 29.64"	84° 49' 15.11"	10631.755	194596.771	162420.643	392692.500
402 stem	North-east of Consiton	46° 36' 24.95"	80° 36' 28.65"	19604.438	352365.802	299062.872	729513.292
402 whorl	North-east of Consiton	46° 36' 24.95"	80° 36' 28.65"	14931.046	267235.500	227499.263	553664.938
101 stem	North of Thessalon off Hwy 129	46° 18' 38.77"	83° 30' 22.7"	9828.053	180094.267	148951.301	360060.171
101 whorl	North of Thessalon off Hwy 130	46° 18' 38.77"	83° 30' 22.7"	9702.193	176931.298	147105.202	354584.890
217 stem	North of Glendale (north-east of Wabos)	46° 50' 45.05"	84° 2' 45.8"	14130.565	262772.902	215031.999	519298.150
217 whorl	North of Glendale (north-east of Wabos)	46° 50' 45.05"	84° 2' 45.8"	13479.644	247284.100	204944.595	494478.306
212 stem	South end of Lake Superior Provincial Park	47° 22' 10.76"	84° 41' 59.68"	10634.597	193835.767	161016.233	388238.463
212 whorl	South end of Lake Superior Provincial Park	47° 22' 10.76"	84° 41' 59.68"	5493.112	99877.535	83274.869	200998.504
140 stem	North-west Cochrane	49° 34' 16.16"	81° 27' 58.85"	7497.028	129953.850	112329.849	268435.556
140 whorl	North-west Cochrane	49° 34' 16.16"	81° 27' 58.85"	5917.283	101828.748	88399.701	211200.002
139 stem	North-east of Kapuskasing	49° 54' 43.31"	81° 51' 30"	15387.189	267378.344	231145.555	553796.444
139 whorl	North-east of Kapuskasing	49° 54' 43.31"	81° 51' 30"	8602.289	150444.805	129651.852	310290.647
611 stem	North-west of Espanola	46° 23' 0.08"	81° 56' 1.16"	15586.433	331976.917	246271.438	632251.121
611 whorl	North-west of Espanola	46° 23' 0.08"	81° 56' 1.16"	9280.788	189326.703	145176.742	367449.803
226 stem	North-west of Blind River	46° 11' 18.06"	82° 58' 21.42"	18332.684	336881.448	280925.460	679481.608
226 whorl	North-west of Blind River	46° 11' 18.06"	82° 58' 21.42"	16474.758	302655.453	251774.602	608859.444
224 stem	North east of Bruce Mines	46° 23' 19.23"	83° 43' 44.56"	16509.046	303476.906	252776.395	613044.712
224 whorl	North east of Bruce Mines	46° 23' 19.23"	83° 43' 44.56"	16749.307	307867.203	255990.356	620926.494

Appendix f. Blank Correction and Mass Discrimination Example Calculations

The following are the mass discrimination factors taken into account using for the sample signals $Pb_{204\text{-}208}$ and the corresponding blank signals Pb_{204b}-Pb_{208b}

$Pb_{204c}=Pb_{204}-Pb_{204b}$

$Pb_{206c}=Pb_{206}-Pb_{206b}$

$Pb_{207c}=Pb_{207}-Pb_{207b}$

$Pb_{208c}=Pb_{208}-Pb_{208b}$

The terms $Pb_{204,}$ $Pb_{206,}$ Pb_{207} and Pb_{208} are the sample signals, $Pb_{204b,}$ $Pb_{206b,}$ Pb_{207b} and Pb_{208b} are the blank signals and $Pb_{204c,}$ $Pb_{206c,}$ Pb_{207c} and Pb_{208c} are the blank corrected signals. The isotope ratios corrected for mass discrimination effects are obtained from the following equations:

$^{206}Pb{:}^{204}Pb = (Pb_{206c}/Pb_{204c})[\ 16.938\ /(Pb_{206s}/Pb_{204S})]$

$^{207}Pb{:}^{204}Pb = (Pb_{207c}/Pb_{204c})[\ 15.491\ /(Pb_{207s}/Pb_{204S})]$

$^{208}Pb{:}^{204}Pb = (Pb_{208c}/Pb_{204c})[\ 36.721\ /(Pb_{208s}/Pb_{204S})]$

The terms (Pb_{206c}/Pb_{204c}), etc., are the isotope ratios uncorrected for mass discrimination effects. The term (Pb_{206s}/Pb_{204s}) are the isotope ratios values from the NIST SRM 981 standard that was ran. The numbers correspond to the certified NIST SRM 981 corresponding isotope ratio values.

Appendix g. Mass bias corrected ICP MS isotope ratios for lichen

Sample ID (Average)	Location	*Corrected Pb206/Pb207	* Corrected Pb208/Pb206	* Corrected Pb207/Pb208	* Corrected Pb208/Pb204	*Corrected Pb207/Pb206
411 stem	North of Cartier, Division Lake	1.193	2.063	0.406	38.472	0.838
411 whorl	North of Cartier, Division Lake	1.168	2.104	0.406	38.313	0.856
622 stem	North-east of Westree	1.147	2.119	0.411	37.565	0.872
622 whorl	North-east of Westree	1.140	2.126	0.412	37.480	0.877
141 stem	Greenwater Provincial Park	1.101	2.178	0.417	36.346	0.908
141 whorl	Greenwater Provincial Park	1.091	2.189	0.418	36.170	0.916
310 stem	South of Timmins	1.084	2.198	0.419	36.039	0.922
310 whorl	South of Timmins	1.091	2.187	0.419	36.151	0.917
610 stem	North of Webbwood	1.179	2.075	0.409	38.273	0.848
610 whorl	North of Webbwood	1.175	2.079	0.410	38.261	0.851
311 stem	Coming into Timmins	1.095	2.216	0.412	36.775	0.913
311 whorl	Coming into Timmins	1.066	2.228	0.420	35.170	0.938
203 stem	Kiosk	1.172	2.091	0.408	38.437	0.853
203 whorl	Kiosk	1.166	2.092	0.409	38.165	0.857
307 stem	North of Timmins, Hersey Lake trails	1.049	2.266	0.420	35.736	0.953
307 whorl	North of Timmins, Hersey Lake trails	1.063	2.294	0.410	36.894	0.941
222 stem	North-east of Sault Ste. Marie	1.192	2.051	0.409	38.087	0.839
222 whorl	North-east of Sault Ste. Marie	1.185	2.062	0.409	38.187	0.844
216 stem	North of Glendale	1.258	1.958	0.410	38.685	0.804
216 whorl	North of Glendale	1.198	2.040	0.409	38.308	0.834
223 stem	South-east of Echo Bay	1.295	1.950	0.396	40.553	0.772
223 whorl	South-east of Echo Bay	1.271	1.967	0.400	39.781	0.787
404 stem	West of Whitefish	1.166	2.116	0.405	38.722	0.858
404 whorl	West of Whitefish	1.161	2.116	0.407	37.877	0.862
306 stem	North of Timmins, off of Big Water lake	1.049	2.260	0.421	35.586	0.953
306 whorl	North of Timmins, off of Big Water lake	1.046	2.263	0.422	35.429	0.956

405 stem	North-west of Whitefish	1.174	2.095	0.406	38.293	0.852
405 whorl	North-west of Whitefish	1.170	2.102	0.406	38.390	0.854
406 stem	North-west of Azilda	1.168	2.115	0.404	38.609	0.856
406 whorl	North-west of Azilda	1.160	2.124	0.405	38.469	0.862
202 stem	North of Bonfield off Hwy 17	1.182	2.079	0.406	38.349	0.846
202 whorl	North of Bonfield off Hwy 18	1.184	2.068	0.408	38.115	0.845
120 stem	South of Wawa off Hwy 17	1.188	2.281	0.369	42.395	0.842
120 whorl	South of Wawa off Hwy 18	1.189	2.056	0.409	38.303	0.841
240 stem	South of Eliot Lake	1.196	2.051	0.407	38.429	0.836
240 whorl	South of Eliot Lake	1.189	2.059	0.408	37.917	0.841
116 stem	North end of Lake Superior Provincial Park	1.187	2.065	0.408	38.261	0.842
116 whorl	North end of Lake Superior Provincial Park	1.187	2.062	0.408	38.292	0.843
402 stem	North-east of Consiton	1.167	2.116	0.405	38.578	0.857
402 whorl	North-east of Consiton	1.164	2.117	0.406	38.443	0.859
101 stem	North of Thessalon off Hwy 129	1.190	2.059	0.408	38.276	0.841
101 whorl	North of Thessalon off Hwy 130	1.183	2.064	0.409	38.183	0.845
217 stem	North of Glendale (north-east of Wabos)	1.202	2.035	0.408	38.395	0.832
217 whorl	North of Glendale (north-east of Wabos)	1.194	2.050	0.408	38.380	0.837
212 stem	South end of Lake Superior Provincial Park	1.192	2.054	0.408	38.196	0.839
212 whorl	South end of Lake Superior Provincial Park	1.187	2.064	0.408	38.283	0.842
140 stem	North-west Cochrane	1.145	2.118	0.412	37.462	0.873
140 whorl	North-west Cochrane	1.137	2.125	0.414	37.243	0.880
139 stem	North-east of Kapuskasing	1.142	2.122	0.412	37.554	0.876
139 whorl	North-east of Kapuskasing	1.145	2.113	0.413	37.638	0.873
611 stem	North-west of Espanola	1.333	1.943	0.386	41.942	0.750
611 whorl	North-west of Espanola	1.290	1.980	0.391	40.938	0.775
226 stem	North-west of Blind River	1.186	2.058	0.409	38.323	0.843
226 whorl	North-west of Blind River	1.187	2.058	0.409	38.241	0.843
224 stem	North east of Bruce Mines	1.185	2.066	0.408	38.424	0.844
224 whorl	North east of Bruce Mines	1.187	2.063	0.408	38.360	0.842

Appendix h. Standard SRM 981, 982 and digested 982 during lichen analysis

Sample ID	*Pb206/Pb207 1.093324 (certified value)	*Pb208/Pb206 2.163542 (certified value)	*Pb207/Pb208 0.422752 (certified value)	*Pb208/Pb204 36.64469 (certified value)	*Pb207/Pb206 0.914642 (certified value)
SRM 981	1.092234	2.16354	0.42275	36.64469	0.915554725
SRM 981	1.091024985	2.172033854	0.42156345	36.91580721	0.916569294
SRM 981	1.092323796	2.158703781	0.423662271	36.51098627	0.915479461
SRM 981	1.092247878	2.170110628	0.422374146	36.72322349	0.915543092
SRM 981	1.09134045	2.152293038	0.425307052	36.34021343	0.916304349
SRM 981	1.092088597	2.171303882	0.421294467	36.92887999	0.915676624
SRM 981	1.091704038	2.15849881	0.423943037	36.56977628	0.915999177
SRM 981	1.090681288	2.169628892	0.42216373	36.60346137	0.916858124
SRM 981	1.094058216	2.158518044	0.423027033	36.78432619	0.914028144
SRM 981	1.091290393	2.171648773	0.421535658	36.76680596	0.916346379
SRM 981	1.091207185	2.164367502	0.422986021	36.72481465	0.916416253
SRM 981	1.092045835	2.165336035	0.422472132	36.6347229	0.91571248
SRM 981	1.099729718	2.147130375	0.423428644	36.36253272	0.909314338
SRM 981	1.095462186	2.1655057	0.421121597	36.7432586	0.912856704
SRM 981	1.089915839	2.172760925	0.421851241	36.98021373	0.917502035
SRM 981	1.094167367	2.157895912	0.423106782	36.61769647	0.913936962

Sample ID	*Pb206/Pb207 2.141003 (certified value)	*Pb208/Pb206 1.000159 (certified value)	*Pb207/Pb208 0.466996 (certified value)	*Pb208/Pb204 36.744318 (certified value)	*Pb207/Pb206 0.4670707 (certified value)
SRM 982	2.132094318	1.006469202	0.465540356	37.21365167	0.469022403
SRM 982	2.138218246	0.997640394	0.468315121	36.68537391	0.467679107
SRM 982	2.148099147	0.992209217	0.468712631	36.50702733	0.465527861
SRM 982	2.1436289	0.993689761	0.468990254	36.51604309	0.466498656
SRM 982	2.159803625	0.98981475	0.467300289	36.45416071	0.463005057
SRm 982	2.178145594	0.973541339	0.471110662	36.34062424	0.459106133
SRM 982	2.177362116	0.980011097	0.468168922	36.71981066	0.459271332
SRM 982	2.185448466	0.973542044	0.469536064	36.52488603	0.457571988
SRM 982	2.152583411	0.992889959	0.467415521	36.54420634	0.464558072
SRM 982	2.160324059	0.986526252	0.468745043	36.23544725	0.462893516
SRM 982	2.140080991	0.997971131	0.467752426	36.58644521	0.467272035
SRM 982	2.139196053	0.998462592	0.468103862	36.73272688	0.467465335
SRM 982	2.113818866	1.010137863	0.467859893	36.4382372	0.473077432
SRM 982	2.156948572	0.991214265	0.467258169	36.51574386	0.463617915
SRM 982	2.13842102	0.99764406	0.468268993	36.81118828	0.46763476
SRM 982	2.148560982	0.994086524	0.467726919	36.56577811	0.465427795

SRM 982	2.13744298	0.997918152	0.468354585	36.48316353	0.467848738

Sample ID	*Pb206/Pb207 2.141003 (certified value)	*Pb208/Pb206 1.000159 (certified value)	*Pb207/Pb208 0.466996 (certified value)	*Pb208/Pb204 36.744318 (certified value)	*Pb207/Pb206 0.4670707 (certified value)
Digestion SRM 982 1	2.123305592	1.012661375	0.46460886	37.45902282	0.470963767
Digestion SRM 982 2	1.245505497	1.884000375	0.425733282	36.20051727	0.802886862
Digestion SRM 982 3	2.153669263	0.995082336	0.46615056	37.01333507	0.464323848
Digestion SRM 982 4	2.148041107	0.995719004	0.467073096	36.72393552	0.465540439
Digestion SRM 982 5	2.134769498	1.001983769	0.467038369	36.69960359	0.468434649
Digestion SRM 982 6	2.138874008	1.0025064	0.466285869	36.83688679	0.46753572
Digestion SRM 982 7	2.127443171	1.006257959	0.466656093	37.04482873	0.470047808
Digestion SRM 982 8	2.129487012	1.004869821	0.46685223	36.88243424	0.469596666

Appendix I. Varian ICP 819 Operating Parameters

	Parameters	Settings
Gas Flow (L/min)	Plasma Flow	16.5
	Auxiliary Flow	1.65
	Nebulizer Flow	0.23
	Sheath Flow	1
RF	RF Power (kW)	1.35
Manual Sample Intruducion	Spray Chamber (°C)	3
	Pump Rate (rpm)	4
Ion Options (V)	1st Extrction Lens	-1
	2nd Extrction Lens	-265
	3rd extraction Lens	-218
	Corner Lens	-291
	Mirror Lens Left	16
	Mirror Lens Right	26
	Mirror Lens Bottom	32
	Entrance Lens	0
	Entrance Plate	-31
	Fringe Bias	-2.6
	Pole Bias	0
Quadrupole Scan	Scan Mode	Peak Hopping
	Dwell Time (ms)	5, 5, 9, 5, 6, 6, 6
	Points Per Peak	1
	Scans/Sweeps	600
	Replicates per Sample	10